ADSORPTION AND SELF-HYDROGENATION OF BUTA-1,3-DIENE ON SILICA-SUPPORTED METAL CATALYSTS

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TO

PATRICK AND IRENE LAVERTY

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CHAPTER ONE

INTRODUCTION

1.1. General Introduction

The catalytic hydrogenation of unsaturated hydrocarbons has been a subject of extensive study since the pioneering work of Sabatier and Senderens (1) at the beginning of the twentieth century. Modern theories of heterogeneous catalysis are based on the work of Langmuir (2) who, in 1916, proposed that the adsorption of at least one of the reactants on to the catalyst surface was necessary before any catalysed reaction could occur.

Atoms exposed on the surface of a solid differ from the atoms in the bulk in that they do not have a full complement of neighbouring atoms with which they can form bonds. The co-ordination number of the surface atom is thus less than that of atoms within the bulk of the solid, and each surface atom must, therefore, possess one or more free valencies, which are capable of forming bonds with foreign atoms or molecules. This process is known as adsorption.

Two types of adsorption have been recognised, physical adsorption and chemical adsorption, usually termed chemisorption.

Physical adsorption is analogous in nature to the van der Waals' forces between molecules in fluids. The bonds formed between a surface and a physically adsorbed molecule are weak, of the order of 20 kJ mol^{-1}. Physical adsorption is readily reversible, and several layers of molecules may be physically adsorbed on to a surface.

Chemisorption involves the formation of chemical bonds between

the surface and the adsorbate. The bond, therefore, is much stronger than that observed in physical adsorption, typically between 40 and 600kJ mol^{-1}, and reversibility can generally only be effected at high temperature. Chemisorption often requires an activation energy, and only a single monolayer of atoms or molecules may be chemisorbed on a surface. Chemisorption is often seen to be a dissociative process, particularly in the cases of hydrogen, oxygen, nitrogen and some hydrocarbons.

Lennard-Jones (3) has made a clear distinction between physical adsorption and chemisorption by a consideration of the potential energy involved in each process. The differences in potential energy between the two processes is illustrated in figure 1.1. for the case of a diatomic molecule undergoing physical adsorption, and dissociative chemisorption.

Thermodynamically, chemisorption is a spontaneous process and is therefore accompanied by a decrease in the Gibb's free energy, that is, ΔG is negative. As the process of adsorption involves the ordering of molecules, previously in a fluid state, on the surface of a catalyst, it must involve a decrease in entropy. Consequently, since $\Delta G = \Delta H - T\Delta S$, adsorption must be an exothermic process, that is, ΔH_{ads} is negative.

The strength of the surface bond, and hence the heat of adsorption ΔH_{ads}, depends both on the nature of the adsorbate and the adsorbent. The heat of adsorption has also been found to be dependent on the degree of surface coverage (θ), and, in general, decreases markedly (4) with increasing surface coverage.

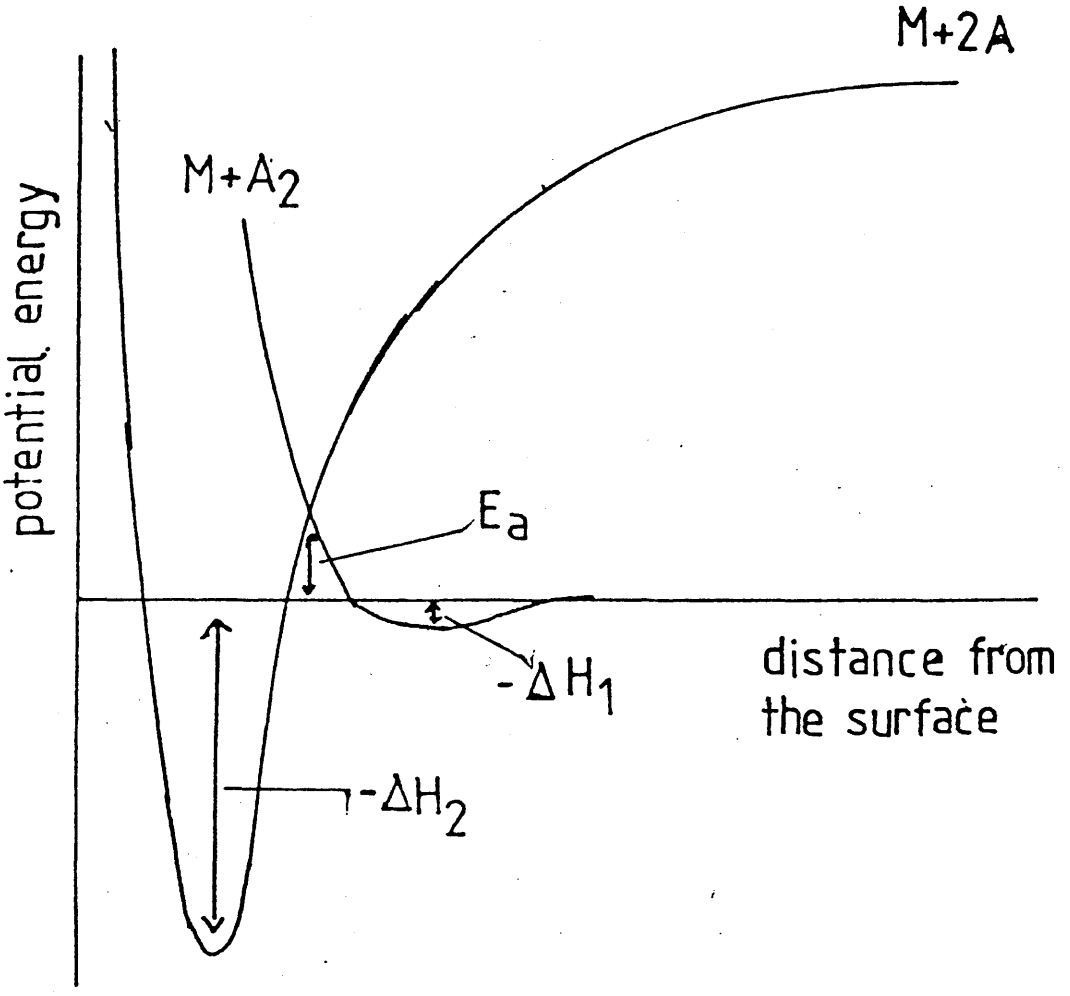


Figure 1.1.

Lennard Jones Diagram for Adsorption of Diatomic Molecule

$-\Delta H_1$ heat of physical adsorption; $-\Delta H_2$ heat of chemisorption;

E_a Activation energy for chemisorption.

Three explanations, advanced to explain this behaviour, have been reviewed by Gundry and Tompkins (5);

(a) the heterogeneous nature of the adsorbent surface, arising from point defects and dislocations (4), and from the exposure of various crystal faces, each with their own geometry, on the surface,

(b) repulsions between adjacently adsorbed molecules (6), which might be expected to become more important as the surface coverage increases, and

(c) electron transfer between the adsorbent and the adsorbate.

The concept of surface heterogeneity is believed to be the most satisfactory explanation of the variation of the heat of adsorption with surface coverage in discussions of adsorption on transition metals. The heterogeneity of metal surfaces with respect to adsorption has been demonstrated (7) for hydrogen on nickel.

The existence of heterogeneity suggests that reaction may take place, not over the whole catalyst surface, but at special 'active sites', as first proposed by Taylor (8). The role of defects and dislocations as centres of reactivity and possible active sites has been reviewed by Thomas (9), and the difference in catalytic behaviour of different crystal faces has been demonstrated by a variety of techniques, including the study of reaction rates on single crystals (10), Field Emission Microscopy (11) and Low Energy Electron Diffraction coupled with Auger Electron Spectroscopy (12).

Somorjai and Blakely (13) have used the latter technique to demonstrate the importance of kinked and stepped crystal faces of platinum in the dehydrogenation and hydrogenolysis of cyclohexane and cyclohexene. Although the surface was rapidly covered by carbon overlayers, these authors suggested that the steps and kinks, which they propose are active sites for bond fission, are left bare.

A possible role for the carbon overlayers described by Somorjai and his coworkers has been proposed by Thomson and Webb (14). These authors have proposed a general mechanism for the hydrogenation of unsaturated hydrocarbons by hydrogen transfer between an adsorbed hydrocarbon surface species, M - CxHy, and an adsorbed olefin. This interpretation suggests that a knowledge of the modes of adsorption and retention of hydrocarbon species on metal catalysts is a required basis for a discussion of hydrogenation.

1.2. The Chemisorption of Unsaturated Hydrocarbons

The chemisorption of hydrocarbons on metal catalyst surfaces plays a very important role in the catalytic process, as it is generally accepted that the chemisorption of hydrocarbons precedes their hydrogenation. It is also accepted that the nature of the adsorbed state has a direct bearing on the mechanism.

Many techniques have been applied in the study of adsorption. Infra-red spectroscopy, first developed by Eischens and Pliskin (15,16), has been widely used. Morrow and Sheppard (17,18) have shown that ethylene is dissociatively adsorbed on silica-supported platinum and nickel. Spectra recorded following subsequent hydrogenation of the adsorbed ethylene showed that polymerisation to

adsorbed n-butyl species which are retained on the surface had occurred.

Further work by Avery (19) showed that linear mono-olefins form multiply bonded, highly dehydrogenated, dissociatively adsorbed species on silica-supported palladium. Buta-1,3-diene did not give a spectrum on initial adsorption. Since no infra-red absorption could therefore be attributed to C-H bonds, this was interpreted as indicating that the adsorbed butadiene was completely dehydrogenated. Following hydrogenation of the adsorbed butadiene, a spectrum, richer in bonds attributable to $-CH_2$ groups than in $-CH_3$, was recorded indicating that polymerisation to a strongly adsorbed $(C_4)_n$ species had occurred.

Pearce and Sheppard (20) have, however, pointed out that molecular vibrations which occurred in the plane of the surface would not contribute strongly to the infra-red spectrum, as the change in the dipole moment of the adsorbed molecule caused by the vibration (which must be non-zero if the vibration is to be infra-red active), would be equalised by an induced dipole moment change within the bulk metal. Therefore, the absence of a detectable infra-red spectrum for buta-1,3-diene adsorbed on silica-supported palladium would not necessarily mean that the adsorbed buta-1,3-diene (hereafter referred to as butadiene) was totally dehydrogenated.

The polymeric residues indicated by infra-red spectroscopy appear to be retained on the catalyst after hydrogenation. The existence of residual species on a catalyst surface has also been demonstrated by stoichiometric balance (21,22), field emission

microscopy (23), low energy electron diffraction (24) and by the use of ^{14}C as a radiotracer (25 - 28).

Thomson and Webb and their coworkers (25 - 28) have used ^{14}C to demonstrate the co-existence of at least two modes of adsorption for ethylene on various alumina- and silica-supported metals,at ambient temperature and above. Cormack et al. (25) showed that when ^{14}C-ethylene is adsorbed on to alumina-supported Pd, Pt, Ru,Rh, Ni and Ir catalysts, only a fraction of the initially adsorbed ethylene can be removed by molecular exchange with non-radioactive ethylene, by evacuation or during the subsequent hydrogenation of ethylene-hydrogen mixtures. It was suggested that the species retained was dissociatively adsorbed ethylene, whereas the species removed during hydrogenation was associatively bonded. Similar results have been reported by Reid et al. (26) for ethylene on silica-supported rhodium, and by Al-Ammar and Webb (28,29,30) for ^{14}C-ethylene and ^{14}C-acetylene on silica-supported metals. These observations have led to the postulate that the retained species in ethylene hydrogenation arises from the formation of multiply bonded hydrogen-deficient surface complexes (31).

Inoue and Yasomuri (32), using ^{14}C radiotracers, have identified four types of adsorbed acetylene on cold worked palladium foil: (a) a fraction which undergoes desorption on evacuation, (b) a fraction which is removed during hydrogenation, (c) a fraction which is not removed during hydrogenation at ambient temperature but which is removed by treatment with hydrogen at 423K and (d), a fraction which is not removed from the surface by reduction at 423K. These authors

considered the type (b) species to be the species responsible for hydrogenation.

Rooney et al. (33,34) have suggested that a π-bonded adsorbed species is active in hydrogenation, and Sheppard and his co-workers (35) have obtained evidence for both a di-σ-bonded and a π-bonded species when ethylene is chemisorbed on hydrogen-precovered silica-supported platinum and palladium catalysts, both of which they claim are easily hydrogenated, the π-bonded species being the more reactive.

Compared with monoolefins, the adsorption of diolefins has been little studied. Infra-red studies carried out by Avery (19) show that butadiene is very strongly adsorbed, and that the adsorbed species is highly dehydrogenated. Most information concerning the probable modes of adsorption of butadiene on supported metal catalysts has come from studies of the gas-phase hydrogenation of butadiene over these catalysts.

Bond and his co-workers (36) carried out the first detailed investigation of the hydrogenation of butadiene on alumina-supported Ru, Rh, Pd, Os, Ir and Pt catalysts. This work has been extended by Wells et al. (37 - 40) to alumina-supported Fe, Co, Ni and Cu and to Rh, Pd, Ir and Pt wires. The gas-phase deuteration of butadiene has also been studied over alumina-supported palladium by Meyer and Buswell (41).

These studies have shown that n-butane and the three n-butenes are formed as initial products on all the catalysts, with the exception of the palladium catalysts, where only the n-butenes are formed.

The extent to which the n-butenes are formed in preference to n-butane is known as the selectivity, which is given by

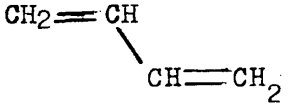
$$S = \frac{\text{total yield of n-butene}}{\text{total yield of n-butene + yield of n-butane}}$$

The other catalysts were not totally selective for butene formation, n-butane being formed in varying amounts as an initial product on alumina-supported Ru, Rh, Ir, Os, Pt, Fe, Co, Ni and Cu (36,38,39) and on Rh, Ir and Pt wires (40).

The distribution of the n-butenes varies with the extent of hydrogenation. But-1-ene is the most abundant of the n-butenes in the initial stages of reaction over all catalysts, but decreases in relative abundance with respect to the but-2-enes as the reaction proceeds. But-1-ene is the major product on all catalysts except Ir/Al_2O_3, where n-butane is the most abundant product (36).

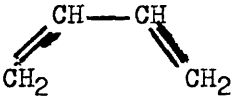
The ratios of trans-but-2-ene to cis-but-2-ene were generally close to unity over most catalysts, but over Pd/Al_2O_3 the ratio was typically about 10, (36) and on a thin Pd film it was found to be temperature dependent (40). Cobalt and nickel catalysts reduced above 673K were found to behave similarly to palladium in giving high (4 - 11) trans:cis ratios (38).

Butadiene exists in the gas-phase in two conformations, (A) and (B) as shown.



syn- (93%)

(A)

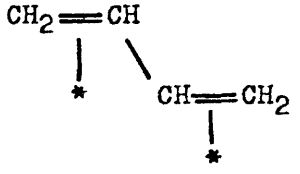


anti- (7%)

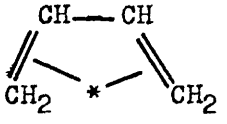
(B)

As butadiene is strongly adsorbed on the catalyst, Bond and his coworkers (36) considered that butadiene was multiply bonded to the catalyst, and proposed a di-π-adsorbed species as the chemisorbed state of butadiene. A tetra-σ-adsorbed species was considered to be unlikely due to the inherent internal strain associated with this species.

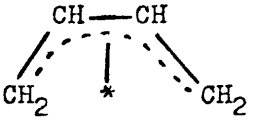
The syn-conformation (A), when di-adsorbed would be required to form bonds with two metal atoms (C). However, in the alternative anti-conformation (B), the double bonds would be more likely to interact with one metal atom, and the double bonds may either retain their individuality (D), or may become delocalised (E) as shown.



(C)



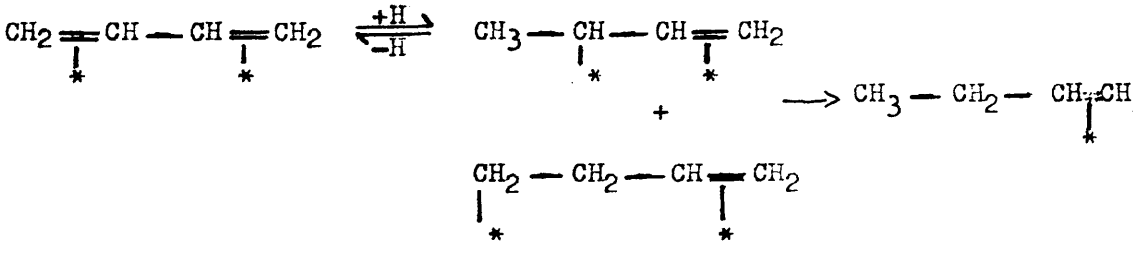
(D)



(E)

It was proposed that but-1-ene was formed by a stepwise 1,2-addition of hydrogen to adsorbed butadiene as shown (1), the conformation of the adsorbed butadiene being unimportant

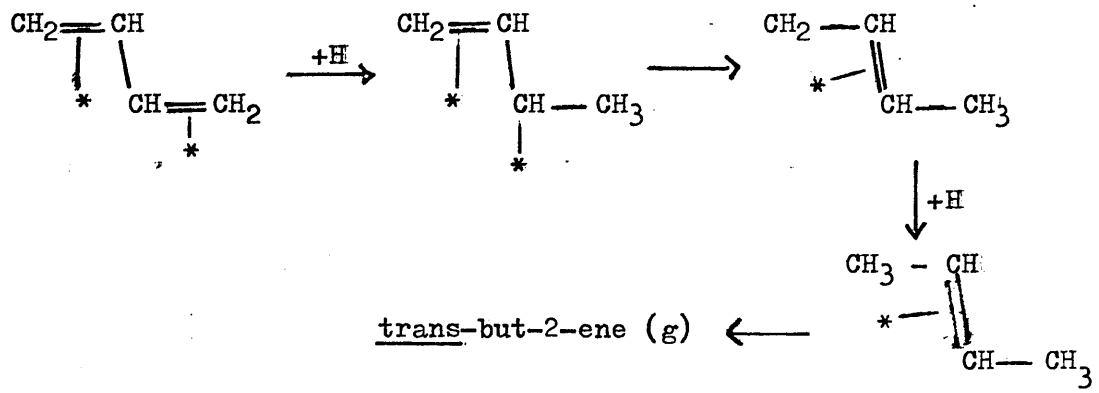
(1)



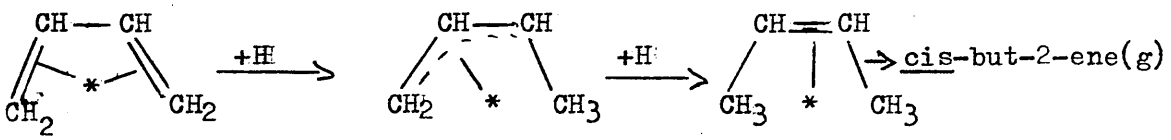
But-2-ene could be formed as an initial product by either 1,4-addition of hydrogen or from the isomerisation of but-1-ene formed in equation (1), or a combination of these processes.

In the proposed direct 1,4-addition of hydrogen to butadiene to form but-2-ene, the conformation of the adsorbed butadiene, and the ability of the adsorbed half-hydrogenated C_4H_7 species to isomerise will play a part in the relative abundances of <u>trans</u>- and <u>cis</u>-but-2-ene in the hydrogenated product. Equations (ii) and (iii) illustrate the hydrogenation of butadiene, adsorbed in the syn- and anti-conformations, to <u>trans</u>- and <u>cis</u>- but-2-ene respectively.

(ii)

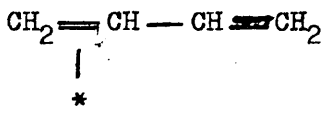


(iii)



As the <u>trans</u>:<u>cis</u> ratio on palladium catalysts (36,39,40) is high, it was considered that on palladium catalysts the two adsorbed conformations of butadiene, (A) and (B), do not readily interconvert, nor do the conformations of the adsorbed half-hydrogenated C_4H_7-species.

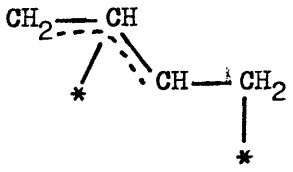
The lower trans:cis ratios observed on other catalysts would seem to indicate that if 1,4-addition occurs, interconversion of the adsorbed states of butadiene or the partially-hydrogenated C_4H_7 species must occur readily. Bond and his coworkers (36) have suggested that, if the adsorbed states of butadiene are accurately represented by species (C) and (D), then interconversion may occur through the mono-π-adsorbed species (F) shown



(F)

Wells (38) has modified this proposal by suggesting that, on those metal catalysts where the trans:cis ratio is close to unity, butadiene is initially adsorbed as the mono-π-adsorbed species (F), before adsorbing further to (C) or (D), which can freely interconvert through (F).

Wells and his coworkers (37) have also found evidence for π-allylic complexes formed by adsorption of butadiene on palladium and palladium-gold catalysts, and have proposed (38,39) that adsorption on palladium involves two non-interconvertible forms, (E) and (G).



(G)

Wells and his coworkers have used these proposed species in proposing two general schemes for butadiene hydrogenation. In the type (A) mechanism, proposed for those metals where the trans:cis ratio is close to unity, the syn- and anti-adsorbed butadiene can readily interconvert through the mono-π-adsorbed species as shown in figure 1.2. This allows the formation of both cis- and trans-but-2-ene from either conformation of butadiene. In the type B mechanism, proposed for those metal catalysts where the trans:cis ratio is high, this interconversion is not easy and therefore the trans-but-2-ene is formed more readily than the cis-but-2-ene, as the syn-conformation of butadiene, from which trans-but-2-ene is formed, is the more abundant of the two conformations of butadiene.

1.3. The Role of the Catalyst Support

The type of catalyst most commonly used in studies of the adsorption and hydrogenation are catalysts in which the metal is dispersed upon a support material such as alumina or silica. The activity of metal catalysts is generally enhanced in supported metal systems compared with powder and filament systems, and supported metals also have greater stability than evaporated metal films. It was originally thought that the support was inert, and that the enhanced activity was due solely to the very much greater metal surface area achieved with supported metal catalysts. For some time now, however, there has been a growing body of evidence to suggest that the support plays a much more important role in catalysis than merely providing a structural framework.

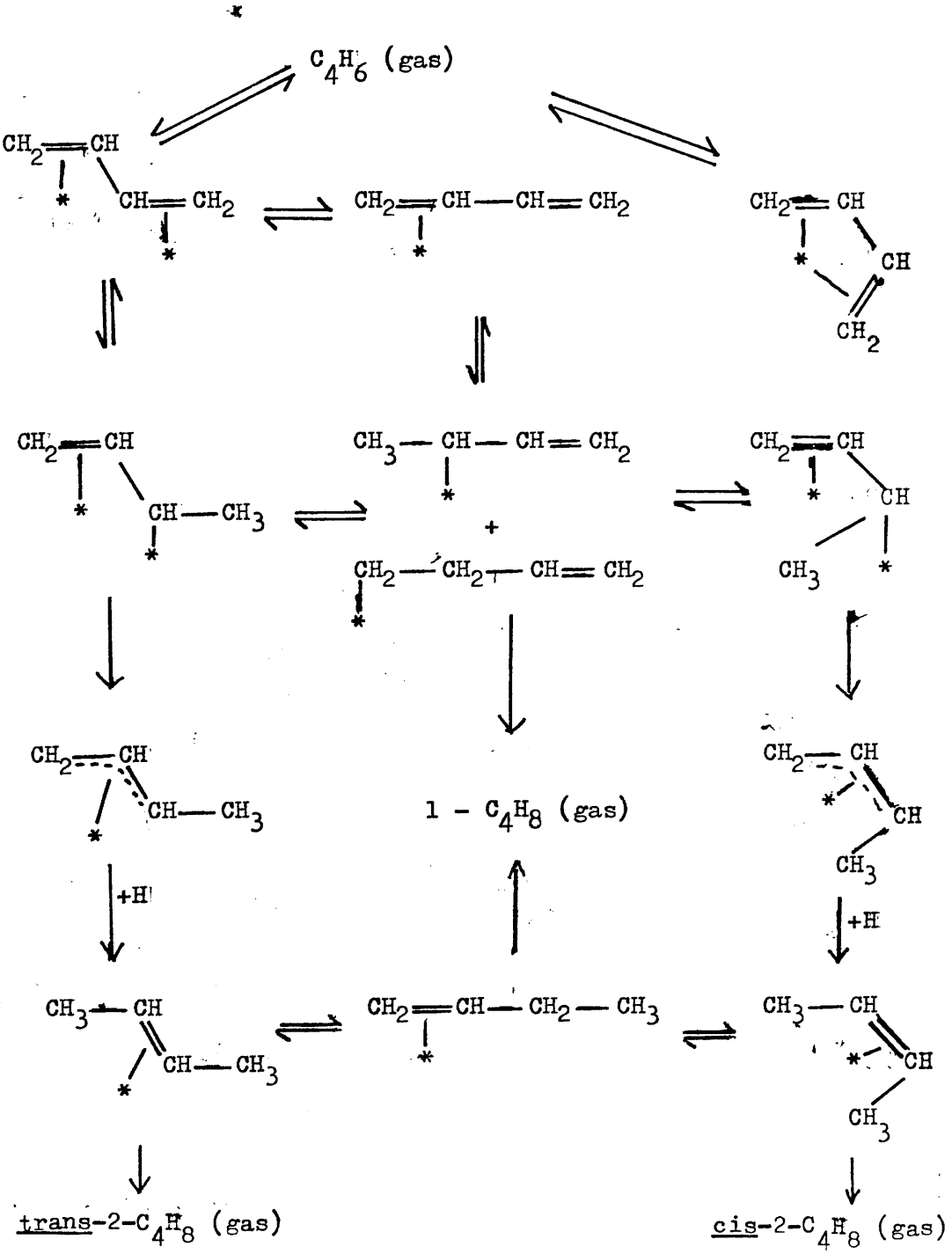


Figure 1.2(a)

Hydrogenation Mechanism Type A.

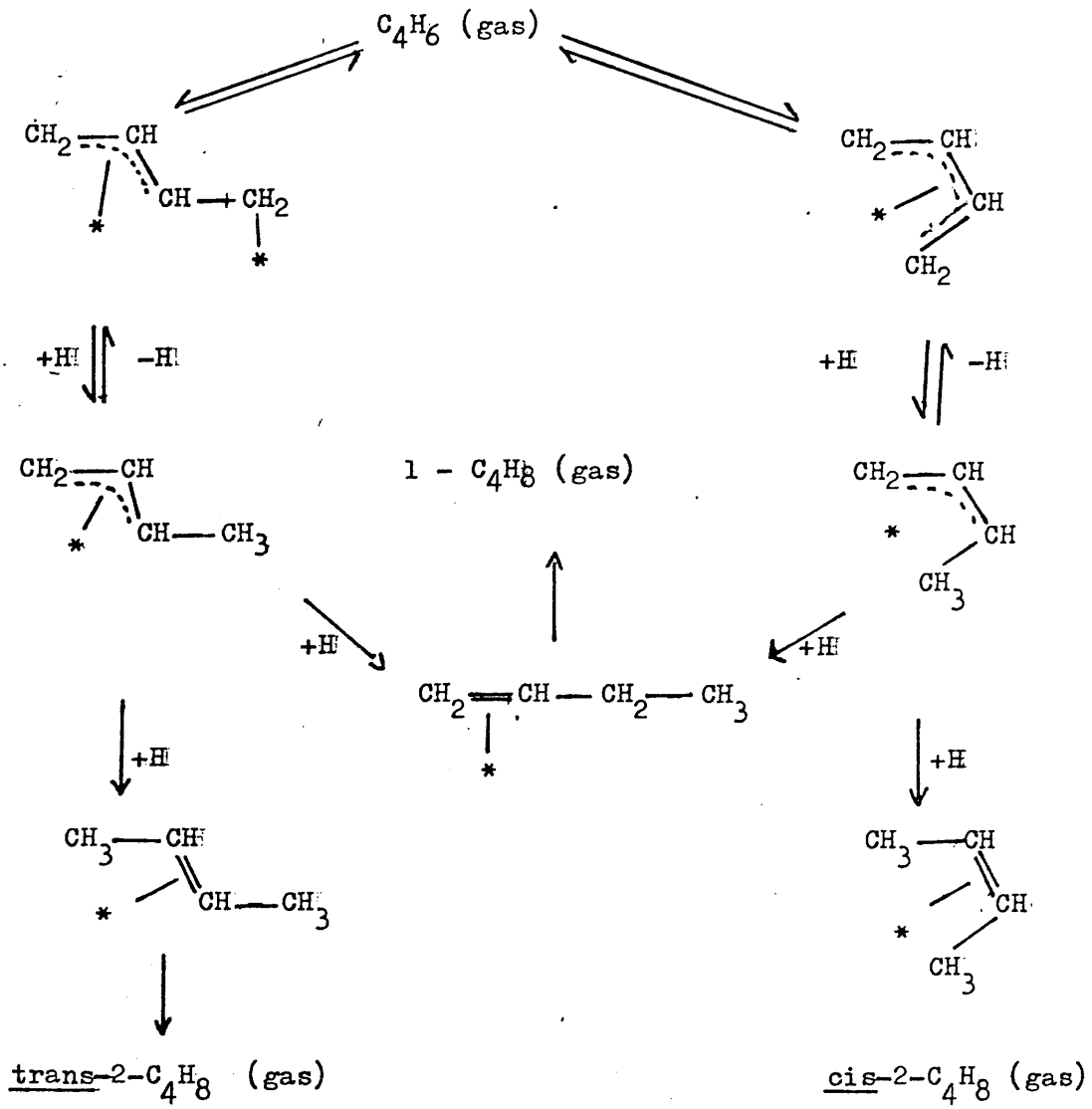


Figure 1.2(b)

Hydrogenation Mechanism Type B

Bond (42), from studies of the reaction of ethylene with deuterium over various types of platinum catalysts, concluded that the support may provide some chemical action. Rooney and Shephard (43) found that platinum supported on α-alumina was much less active than platinum on γ-alumina in catalysing reactions of C_9 alkyl aromatics, whilst Kemball and Hightower (44) found variations in relative reaction rates in a study of the hydrogen exchange and deuteration of p-xylene over platinum when the metal support was changed from α-alumina to γ-alumina and to silica. In a more recent study, Compagnon et al. (45) showed that the initial catalytic activity of Pt/Al_2O_3 for the hydrogenation of cyclopropane was significantly increased by the presence of amorphous alumina as a diluent.

The migration of active intermediates between the metal and the support has been widely accepted as an explanation of the role of the support in determining catalytic activity. This phenomenon, which has been termed spillover, has been considered to be of particular importance with hydrogen on supported metals, and has recently been reviewed by Dowden (46).

Sinfelt and Lucchesi (47) measured the rate of ethylene hydrogenation on a Pt/SiO_2 catalyst mixed with alumina. The rate of hydrogenation was found to be enhanced by the presence of alumina and it was suggested that hydrogen was activated by the metal centres of the Pt/SiO_2 catalyst and then migrated to active centres on the alumina where hydrogenation took place. However, as alumina itself is not active for ethylene hydrogenation (27), it seems more likely that, if hydrogen migration does occur, it will be from the alumina support to the metal.

Direct evidence for the back-migration of hydrogen from support to metal has been obtained by Bond et al (48, 49) who used an alkene tritiation method to characterise a number of supported metal catalysts. Alkene titration of a platinum-H_zWO_3 catalyst at 100°C.(49) yields hydrogen equivalent to a hydrogen:platinum ratio of 277. Since the support alone does not hydrogenate the alkene at this temperature, back-migration of hydrogen must be responsible for the hydrogenation.

Athan and Webb(50) used a radiotracer technique to study the extent of hydrogen spillover. The amount of hydrogen associated with the surface of silica- and alumina-supported platinum catalysts was measured by tritium exchange. The amount of exchangeable hydrogen was in excess of that which could be accommodated on the metal surface alone, and the retention of hydrogen was independent of the platinum concentration over a fifty-fold increase in metal loading. This led to the conclusion that the retained hydrogen was associated with the hydroxyl groups on the surface of the silica and alumina supports. Hydrogenation of ethylene and propylene on these tritium-exchanged catalysts showed tritium incorporation in the products, indicating that the hydrogen associated with these hydroxyl groups was active in hydrogenation. As direct exchange between the hydrocarbon and the support was not observed, indicating that tritium incorporation occured by back-migration to the metal. Similar results have been obtained by Taylor et al (27) and by Campbell and Mooney (51).

An alternative explanation for the excess hydrogen on metal catalysts, that is, in excess of that which can be accommodated on the surface of the metal, may be the occlusion of hydrogen within the

metal. Wells and his coworkers (52) have measured the extent to which the noble metals occlude hydrogen, and Mellor and Wells (53) have suggested that occluded hydrogen may partly account for but-1-ene isomerisation on alumina-supported iridium in the absence of molecular hydrogen, although hydrogen from the alumina support has been shown to be necessary in this reaction (54).

In an attempt to obviate support effects and hydrogen spillover, Wells (55) has studied the occlusion of hydrogen on metal powders by both hydrogen exchange and butene titration. Both methods indicated the presence of hydrogen, and the values obtained by each method for the amount of occluded hydrogen were in good agreement. No account, however, appears to have been taken of the possible self-hydrogenation of but-1-ene in the alkene titration experiments. Wells has suggested that occlusion of hydrogen occurs in cavities within the bulk metal arising from defects within the solid structure of the bulk metal.

Occlusion of hydrogen has also been observed on platinum black (56). Paal and Thomson used radiotracers to show the existence of two types of hydrogen on platinum black, HaI and HaII. HaI is exchangeable with gas phase H_2 and with ethylene and cyclohexene. The exchangeable amount of HaI diminished with time, due to desorption from the metal caused by the helium carrier gas flow, and by migration to hydrocarbon-inaccessable sites to form HaII, which did not exchange with gas-phase hydrogen or hydrocarbon and which was not removed by oxygen. HaII was detected by scintillation counting of catalyst samples immersed in a liquid scintillator. The authors concluded that HaII may be absorbed (occluded) rather than adsorbed.

Spillover of hydrocarbon species has long been implicit in discussions of bifunctional catalysts (57), and Webb and Macnab (58) have shown that the support is active in the hydroisomerisation of but-1-ene or silica-supported rhodium. By progressively poisoning the catalyst with mercury, it was demonstrated that hydrogenation and olefin exchange were much more susceptible to poisoning than was isomerisation. It was suggested that isomerisation occurred on the support, and involved hydrocarbon migration to the support from the metal.

Reid et al. (26, 59) reported that adsorption of ^{14}C-ethylene and ^{14}C-acetylene on silica- and alumina-supported rhodium was a two stage process; a fast primary region, followed by a slower secondary region. ^{14}C-carbon monoxide adsorption showed that the primary adsorption was associated with the metal, and it was observed that adsorption of hydrocarbon in the secondary region could still occur on catalysts precovered with carbon monoxide. It was suggested that the secondary adsorption arose from migration of hydrocarbon from the metal to the support. It was also shown by thermal desorption studies that the secondary adsorbed species were associatively bonded to the surface, whilst the primary adsorbed species were mainly dissociatively bonded, (31, 60).

CHAPTER TWO

THE AIMS OF THE PRESENT WORK

The process of chemisorption is an essential prerequisite to heterogeneous catalysis, and any attempt to explain the mechanism of a catalysed reaction must be based on a sound understanding of the modes of adsorption of the reactants. Self-hydrogenation has often been observed during studies of the adsorption of unsaturated hydrocarbons on metal surfaces, but few workers have made concomitant studies of both these processes.

Whilst the Group VIII metals have been extensively used in studies of the metal catalysed hydrogenation of buta-1,3-diene, relatively few studies have been made of the adsorption and self-hydrogenation of buta-1,3-diene at such catalyst surfaces. The aim of the work described in this thesis was to study the adsorption and self-hydrogenation reactions of buta-1,3-diene over silica-supported platinum, palladium and rhodium catalysts, by investigating:

a) The amounts of hydrocarbon retained on different catalysts, and the extent to which retention varies with temperature on each catalyst.

b) The variation of the product distributions in the self-hydrogenation reactions of buta-1,3-diene on different catalysts at a variety of temperatures.

The role of the support in the self-hydrogenation reaction is also of interest, since hydrogen is normally found to be associated with most commonly used catalyst supports, for example in surface hydroxyl groups on silica and alumina. The extent to which this hydrogen can interact with buta-1,3-diene, and with hydrogen adsorbed

on the catalyst surface following the dissociative adsorption of buta-1,3-diene is of interest in the discussion of self-hydrogenation. This has been investigated by studying:

a) the exchange of hydrogen on the catalyst surface with tritium;

b) the self-hydrogenation reactions of buta-1,3-diene on tritium-exchanged catalysts and the examination of the hydrogenated products for tritium content.

CHAPTER THREE

APPARATUS AND EXPERIMENTAL PROCEDURE

3.1. Introduction

Microcatalytic pulsed-flow reactor systems have been extensively used in catalytic research, especially when the initial interactions between surfaces and reactants are under study. The small pulse size and relatively short contact times give this method an advantage over static systems where the initial reactions may be disguised by the overall reaction going to completion. The pulsed-flow technique is highly suitable when comparing the activities of different catalysts, and when product distributions are to be studied. The technique can also be used in measuring retention, by taking a material balance over a series of pulses. A comparison of the total number of molecules of products and unretained reactant (corrected for cracking or polymerisation, should these processes be observed) with the number of molecules of reactant introduced into the reactor, will show the number of molecules which have been retained.

3.2. The Flow System

A microcatalytic pulsed-flow reactor system similar to the design of Kokes, Tobin and Emmett (61) was used in these studies. A block diagram of this system is shown in figure 3.1.

The flow system was constructed from 3mm o.d. copper tubing with a 'Pyrex' glass catalyst chamber coupled directly to a gas chromatograph, the eluant from which was passed into a gas-flow proportional counter. Figure 3.2 shows a block schematic diagram of the flow system.

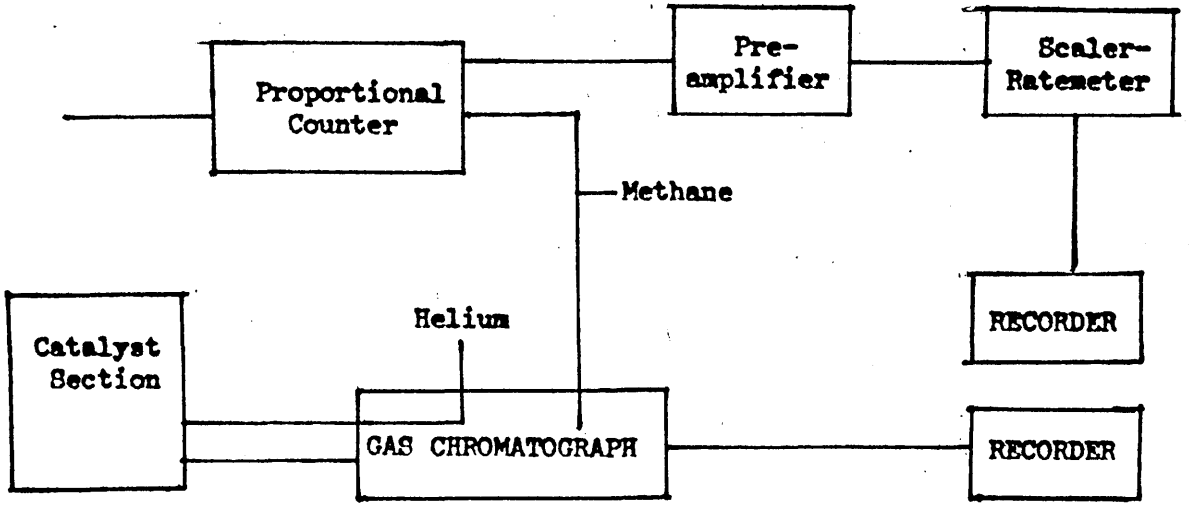


FIGURE 3.1.

Block Diagram of the Flow System

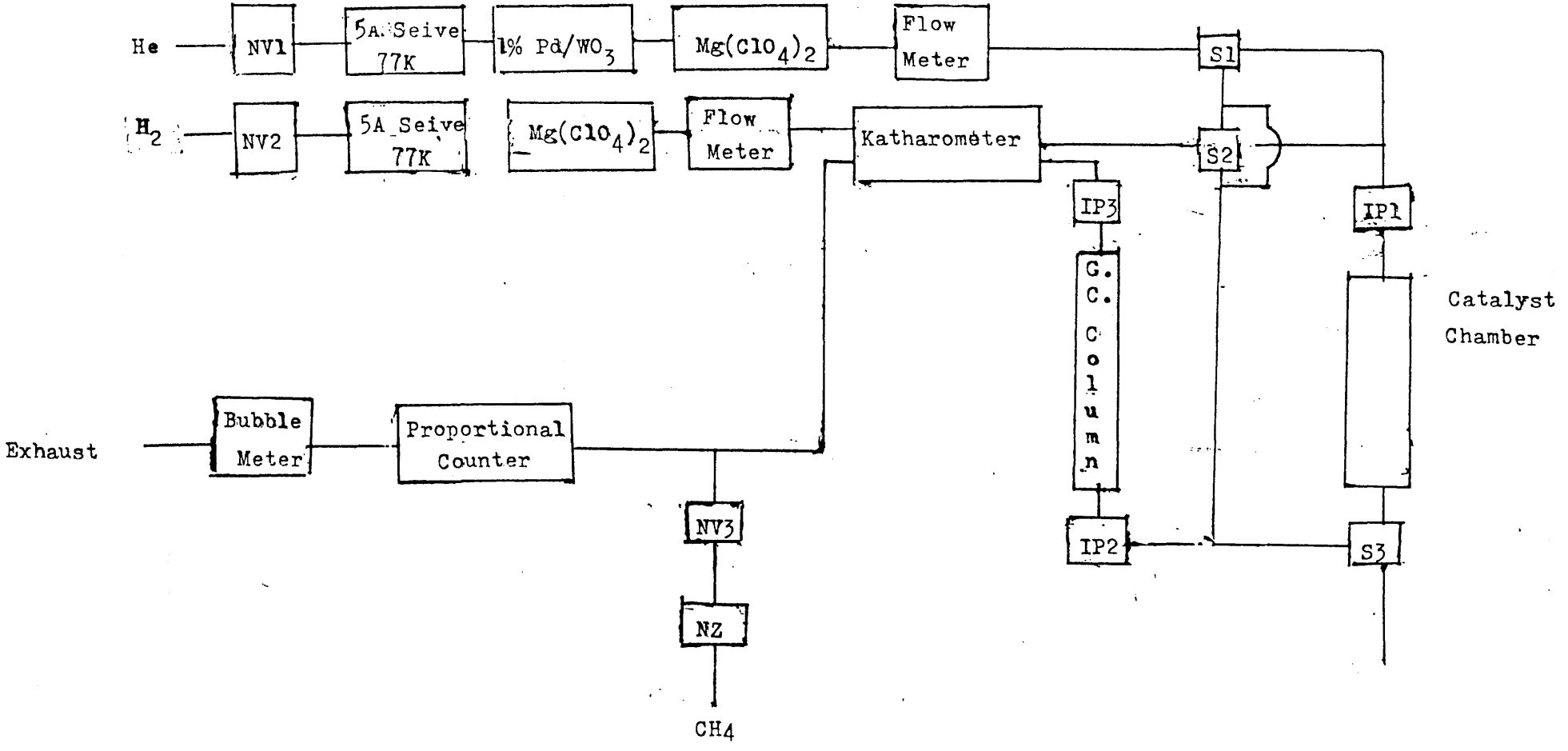


Figure 3.2

The Flow System

NV = Needle valve, S = Switch valve, IP = Injection port, NZ = Nagretti-Zambra valve

The catalyst vessel, which is shown in figure 3.3., was constructed of 'Pyrex' glass and was connected to the metal flow system via graded glass seals and 'Swagelok' connections. The carrier gas flow was directed upwards through the glass sinter into the catalyst bed to prevent compacting of the catalyst bed, since it had been found, during preliminary experiments, that the pressure of the carrier gas tended to compact the catalyst against the sinter when the carrier gas was directed down through the catalyst bed, thus obstructing the flow.

The temperature of the catalyst could be raised both for reduction of the catalyst and for varying the reaction temperature by means of a cylindrical electric furnace surrounding the catalyst chamber. Current to the furnace was supplied via a 'Variac' variable transformer (Zenith Instruments) and the temperature of the catalyst was measured by a Chromel-alumel thermocouple inserted in the thermocouple well of the catalyst chamber. The thermocouple was connected to a 'Comark' electronic thermometer.

Helium (B.O.C. Ltd.) was used as carrier gas. The flow-rate was regulated by a 'Nupro' needle valve and was measured by a calibrated 'Rotameter' gas flow meter. As the scale of the 'Rotameter' did not allow precise determinations of the flow rate, fine adjustments of the needle valve were made using a soap bubble flowmeter, attached to the outlet from the flow system, after an initial setting of the flow rate using the 'Rotameter'. Before entering the flow system, the helium was passed through a 5A molecular sieve trap at 77K to remove impurities and thence through the reference side of the katharometer detector. A rotary switch valve (S2) directed the gas either through

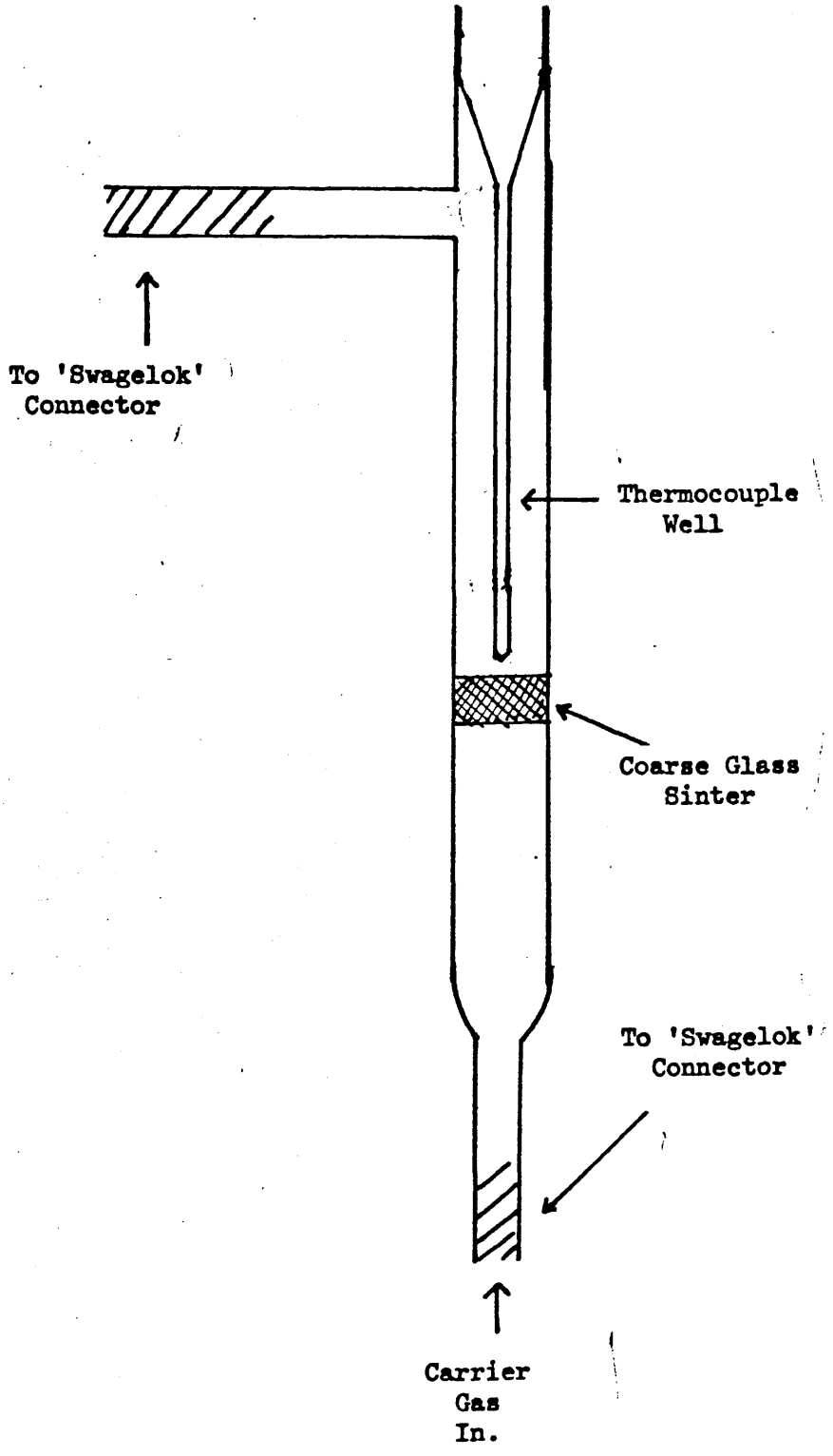


FIGURE 3.3.

The Catalyst Vessel

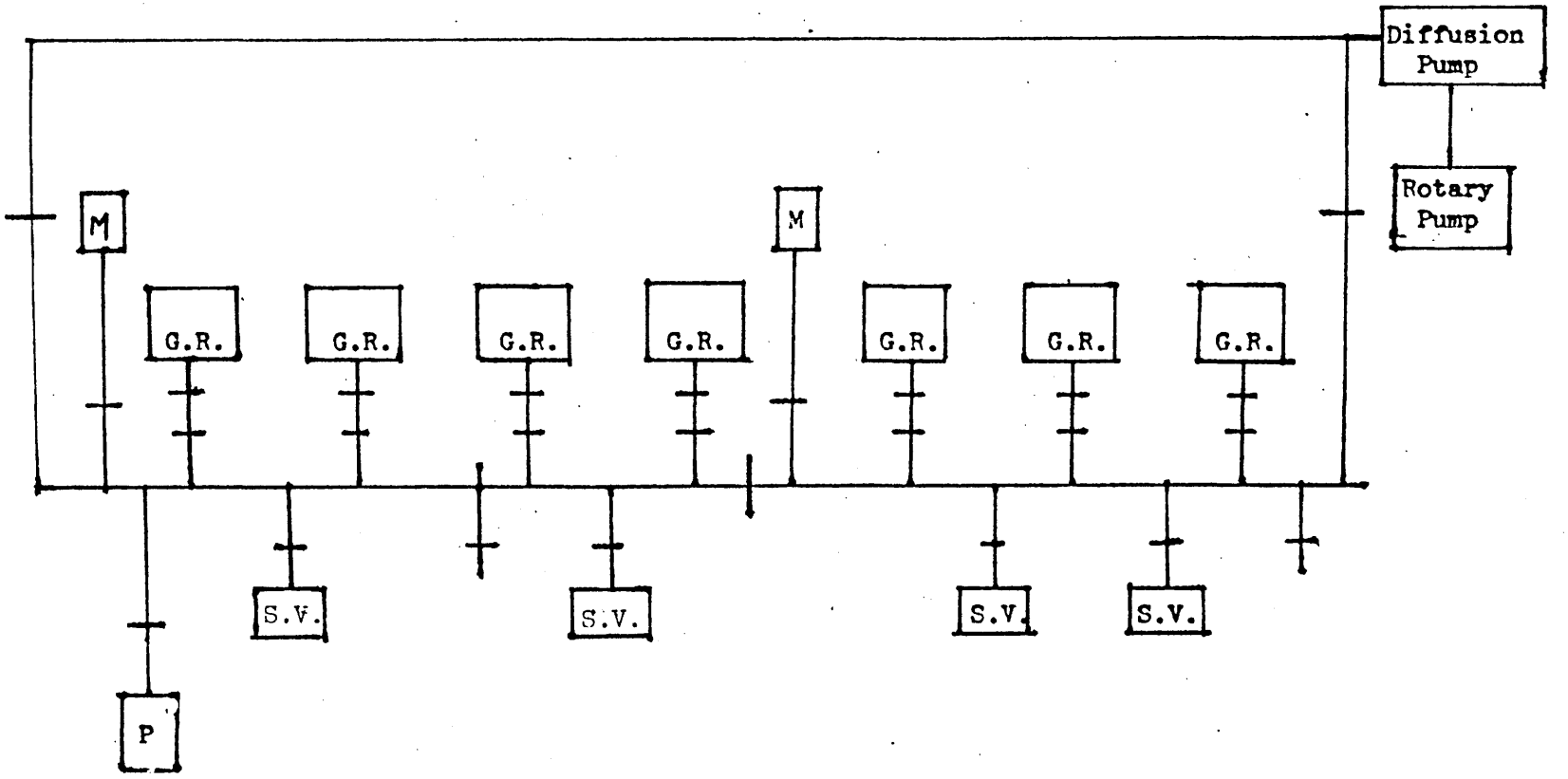
the catalyst chamber and a second switch valve (S3) or through a by-pass circuit, back to the other arm of the katharometer and thence to the gas flow proportional counter. The switch valve S3 enabled hydrogen (air products) for the in-situ reduction of the catalyst, to pass through the catalyst vessel and then to the atmosphere, whilst the carrier gas flow could be maintained through the rest of the system.

The injection ports IP1, IP2, IP3 were sealed with Hamilton 760-05 septum caps (Belmont Instruments).

3.3. The High Vacuum System

The various gases which were used as reactants and as reference gases for the chromatographic analysis were stored in a conventional high vacuum apparatus, which had facilities for storage of several gases, for purification by fractionation, and for transfer of gases to sample vessels at measured pressures greater than atmospheric. A schematic diagram of the high vacuum system is shown in figure 3.4.

The apparatus was maintained at a pressure of 10^{-5} torr or better, by means of a conventional pumping system consisting of a mercury diffusion pump backed by an oil rotary pump, with traps and taps to isolate and protect the diffusion pump when necessary. Two connections were made from the primary manifold (25mm o.d.) to a secondary manifold (12mm o.d.). This secondary manifold was divided into two arms by a 6mm tap and was connected to seven gas reservoirs (G.R.) of various sizes and four sample vessels (SV) fitted with injection ports sealed by 'Suba-seal Number 9' serum caps. Each arm of the secondary manifold had an open-ended manometer and an outlet to the atmosphere, used to fill reservoirs with reactant gases from cylinders. A palladium thimble was incorporated for the purification of cylinder hydrogen. All taps were lubricated with "Apiczon N" vacuum grease.



G.R. = Gas Reservoir
S.V. = Sample Vessel
M = open ended Manometer
P = Palladium thimble.

FIGURE 3.4.

Schematic Diagram of the High Vacuum System

Samples of gas, for use in the flow system were prepared by condensing (or, in the case of tritium, contracting) samples of the gas into a sample vessel so that the sample vessel, on expansion of the gas, contained the gas at a pressure of approximately 1.3 atmospheres.

Gas samples were transferred from sample vessels to the flow system using gas-tight syringes (Hamilton and Company). In most experiments, syringes fitted with Chaney adaptors were used. With Chaney adaptors fitted, a reproducibility of injection size of $\pm$ 0.01% is claimed. When these adaptors are not fitted, a reproducibility of $\pm$ 3% is estimated. Syringes of 0.50ml and 1.0ml capacity were used in the present studies. Prolonged use of the syringes resulted in a loss of 'gas-tightness' due to 'cold flow' of the teflon tip of the plunger. When this problem was apparent, it was overcome by immersing the tips of the plungers in boiling water for one hour.

3.4. Materials

a) The catalysts, which consisted of 5% w/w metal supported on 'aerosil' silica (Degussa Ltd.) were prepared by adding an aqueous solution of the metal chloride, containing the required weight of metal, to an aqueous suspension of the silica support. The excess water was slowly evaporated off and the supported chloride salt finally dried in an air oven at 150°C. When required, the supported salts were reduced <u>in situ</u> in the catalyst vessel under flowing hydrogen at 633K.

b) Helium, which was used as the carrier gas throughout, was passed through a 5A molecular sieve trap cooled to 77K in liquid nitrogen, and dried by passage over $Mg(ClO_4)_2$.

Hydrogen, used in the in situ reduction and regeneration of the catalysts was supplied by Air Products Ltd. This was purified by passing through a 5A molecular sieve trap maintained at 77K by liquid nitrogen, and thence over a 1% Pd/WO_3 catalyst to remove any oxygen, before being finally dried by passage over $Mg(ClO_4)_2$. This drying tube required periodic replacement.

Hydrogen, used in the dilution of tritium gas, was supplied by B.O.C. Ltd., and was purified by passage through a palladium thimble.

Methane, which was used in the counting mixture for the gas flow proportional counter was either Air Products Ltd. 'CP Grade' or '99%', as available. As methane was not allowed to come into contact with the catalyst, its purity was less critical and it was used as supplied.

c) Tritium, was supplied by the Radiochemical Centre, Amersham. The ampoule, containing 1 Ci,was diluted with inactive hydrogen before use.

d) n-Butane, but-1-ene, trans-but-2-ene and cis-but-2-ene were supplied by Matheson and company, and contained no impurities detectable by gas chromatography. These were merely degassed before use.

e) Buta-1,3-diene was supplied by Matheson and company. It was found to contain approximately 0.35% iso-butene and 0.15% but-1-ene. The butadiene was therefore purified by preparative gas chromatography before use.

3.5. The Gas Chromatography System

The gas stream from the catalyst chamber passed into a chromatography column where the various hydrocarbons present in the reactor eluant were separated and then detected by the Gow-Mac katharometer.

The chromatography column consisted of a 14m long, 6mm o.d. copper tube packed with 33% dimethylsulpholane supported on 30/60 mesh firebrick. A carrier gas flow rate of about 60ml min^{-1} was used and this gave adequate separation of the C-4 and C-3 hydrocarbons in the reaction eluant. Complete separation of ethane and ethylene however was not possible on this column and, where appropriate, results are quoted as a combined yield of ethane and ethylene.

The katharometer was connected to a potentiometric recorder which gave a permanent record of the eluted products. Peak areas were measured by either the 'height x width at half-height' method or by a fixed arm planimeter. The planimeter was the method more usually employed, as peaks were generally small and irregular, particularly in the later stages of a set of reactions. Using either method, the inaccuracies were greatest when the measured peak areas were small and efforts were therefore made to produce peaks that were as large as possible by variation of the full scale deflection of the potentiometric chart recorder. As volumes of each eluant diminished, the peaks became less sharp and, at low volumes, accuracy was impaired due to the smallness of the peak area.

To relate peak areas to actual gas volumes, calibration injections of the reactant gas and each of the possible product gases were made at IP2, the reference injection port, and the peak areas measured. The sensitivity of the katharometer was found to vary for each gas, being most sensitive to cis-but-2-ene and least sensitive to methane. Response factors were calculated for each gas so that observed peak areas could be normalised to the equivalent peak area for the same volume of butadiene. These response factors allowed the volumes of

each eluted gas to be calculated by reference to a daily calibration for butadiene. The response factors were calculated from the peak areas observed from the injection of 1ml standard injections of each gas, as described above. A sample calculation is shown below for the case of but-1-ene.

Example:

a 1ml injection but-1-ene - peak area = $736.2mm^2$

a 1ml injection butadiene - peak area = $621.5mm^2$

Then normalising to butadiene $736.2 \times RF = 621.5$

$$RF \text{ (but-1-ene)} = 0.844$$

If, for example, a peak for but-1-ene observed in reactor eluant, was found to have an area of $22.5mm^2$, then

$$\text{volume } (\mu l) = \text{Area} \times \text{Response Factor} \times \frac{\text{Volume of Butadiene Standard } (\mu l)}{\text{Area of Butadiene Standard}}$$

$$\text{volume} = 22.5 \times 0.844 \times \frac{1000}{621.5}$$

$$= 30.55 \mu l.$$

At the start of each experiment, calibration injections of the reactant gas were made at IP2, before reactions were carried out, to demonstrate the reproducibility of the system and to give a standard for the calculation of product volumes.

Daily calibrations were necessary since the reactant gases are injected at ambient temperature and pressure and, thus, day to day variations in these quantities resulted in a daily variation in the precise amount of reactant (μmoles) injected.

From the retention times and peak areas, the nature and quantity of the reaction products was determined. Table 3.1 lists the retention times and the response factors (relative to butadiene) for various gases. Retention times quoted are for injections at the reference port, IP2.

TABLE 3.1.

Retention times (mins.) and response factors relative to butadiene

Gas	Elution time (min.)	Retention time (min.)	Retention time / Retention time 1,3-B	Response Factor.
CH_4	6.0	0.0	0.000	1.961
C_2H_6/C_2H_4	7.25	1.25	0.045	0.815
C_3H_8	8.75	2.75	0.099	1.062
C_3H_6	10.5	4.5	0.162	0.908
n-butane	13.45	7.45	0.267	0.856
but-1-ene	18.1	12.1	0.434	0.844
t-2-butene	21.8	15.8	0.567	0.828
c-2-butene	24.75	18.75	0.673	0.836
buta-1,3-diene	33.85	27.85	1.000	1.000

Flowrate = 60ml min^{-1}, temperature = 290K.

Although the depth of the catalyst bed was kept as small as possible, it was observed that peaks became more diffuse at lower catalyst temperatures (298K or 323K), which interfered with the resolution between trans-but-2-ene and cis-but-2-ene. This chromatographic effect of the catalyst bed was also indicated by a difference in retention times between injections of hydrocarbon made above and below the catalyst. This effect was most noticeable at 298K, where the retention time of butadiene was approximately 31 minutes instead of 27.85 minutes. The effect was not noticeable above 373K.

3.6. The Proportional Counter

A proportional counter based on the design of Schmidt-Bleek and Rowland (62) was constructed for use in the radiochemical experiments. This design has a nominal counting efficiency for tritium of 100%. The design is shown in figure 3.5.

The counter was connected to the outlet from the gas chromatograph, and a proportion of methane was introduced into the gas flow between the chromatograph and the counter, to provide a counting mixture. The ratio of helium to methane in the counting mixture is critical in the operation of the counter, particularly in obtaining a suitable plateau. The proportion of methane was controlled by a Nagretti-Zambra regulator and a Nupro needle valve located on the methane supply line before the junction with the chromatograph exhaust.

The proportional counter was connected to a Nuclear Enterprises SR5 combined scaler and ratemeter via a pre-amplifier. The scaler-ratemeter was adjusted so that it could deliver a high voltage supply

of up to 4kV, and the preamplifier was adjusted to a mode compatible with the proportional counter.

The output from the ratemeter was fed to a 'Servoscribe' potentiometric chart recorder where any activity in the chromatograph eluant was displayed as a peak. In practice, it was usual to use the recorder trace in determining when to start and stop the scaler-timer, which gave a visual read-out of counts and counting time. It was sometimes found that there was inadequate resolution of two radioactive eluants, that is, the second peak appeared before the ratemeter trace had returned to the background level. When this occurred, the scaler-timer was not stopped until background was reached after the second peak. A combined count was recorded, and the activity of each component was assigned after measuring each peak with the fixed-arm planimeter, by dividing the total recorded activity according to the ratio of the peak areas.

3.7. Operation of the Proportional Counter

It had previously been found (63) that the optimal counting conditions, in terms of plateau length and gradient, were achieved with a 10:1 helium to methane ratio. As a helium flow rate of 60ml min^{-1} was required to give adequate chromatographic separation, a methane flow rate of 6ml min^{-1} was used. The methane flow rate was controlled as described above and the combined flow rates measured on a soap-bubble flowmeter attached to the exit from the proportional counter.

With the amplifier of the scaler ratemeter on its integral mode (INT), and the ratemeter set on 1000 cps with a time constant of 4 seconds, an external ^{60}Co source was used to investigate the variation

of count rate against applied voltage for a helium to methane ratio of 10:1. With this counting mixture, a plateau of length 200 volts was regularly achieved. The plateau is shown in figure 3.6.

The operating voltage was selected in the middle of the plateau and, with the other settings as before, the discriminator energy dial was varied through its marked settings from 0.1 to 1.5. The variations in counts with discriminator energy setting are shown in figure 3.7. This also shows a U-shaped curve, with a flat trough extending between 0.5 and 1.2. A setting of 0.8 was used thereafter.

An investigation was carried out to determine whether the various gases expected to appear in the eluant were likely to affect the counting efficiency of the counter. With a ^{60}Co external source in place beside the counter, injections of various amounts of each gas were made at the reference port, IP2. The ratemeter trace was studied to see whether there was any change in the count rate whilst the different gases were passing through the counter. The counting efficiency was found to decrease when volumes of n-butane in excess of 200 μl and volumes of butadiene in excess of 1ml were passing through the counter. As these are both greatly in excess of the volumes to be expected in any of the radiochemical experiments, no corrections were necessary.

The counter often acted as a source of radio-frequency noise, which interfered occasionally with counting. This was remedied by reducing the lengths of the electrical cables connecting the counter, the pre-amplifier and the scaler-ratemeter to the base minimum, and by encasing the counter and pre-amplifier in copper gauze. The copper gauze was then earthed.

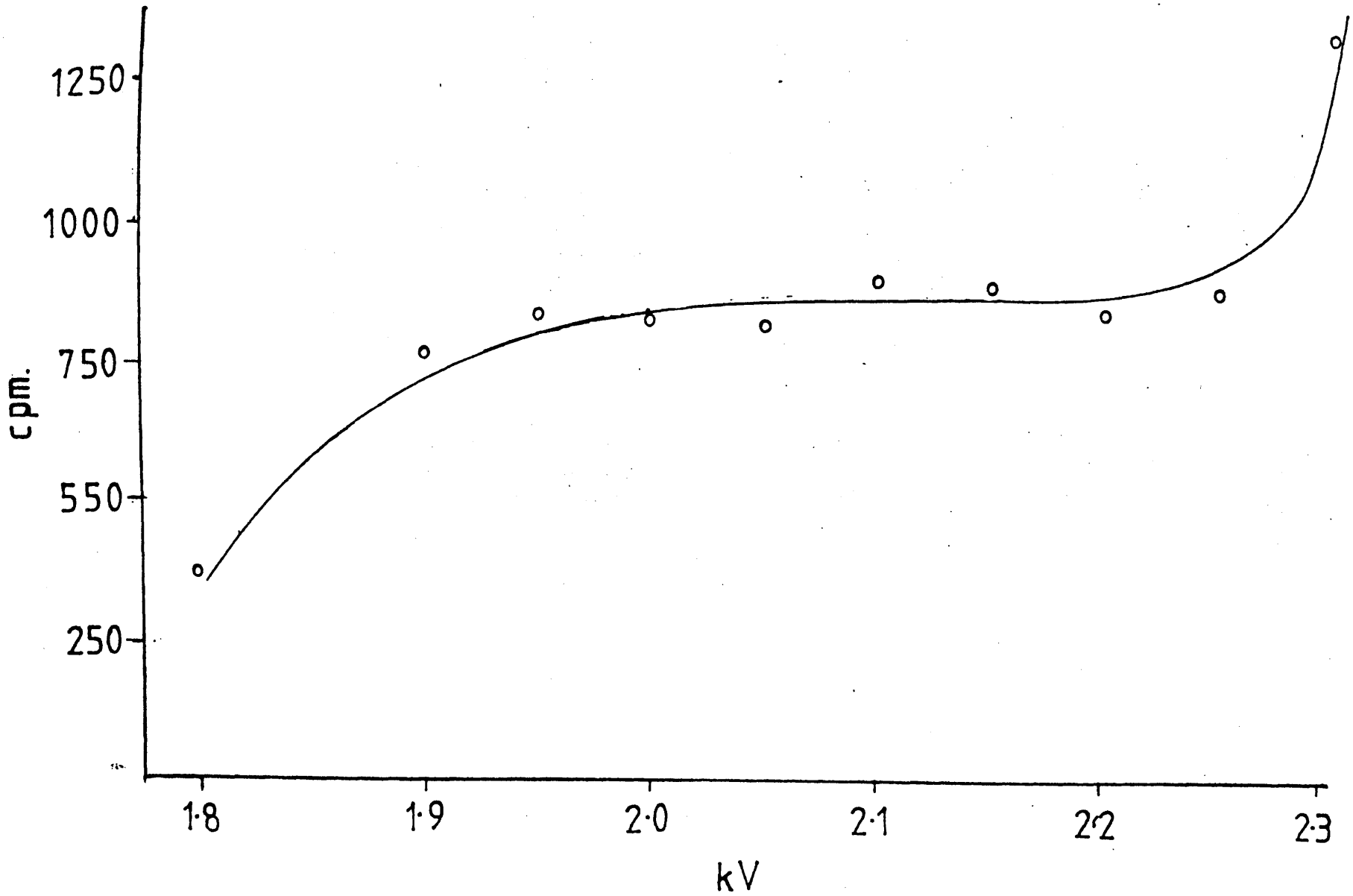


Figure 3.6. The Plateau.

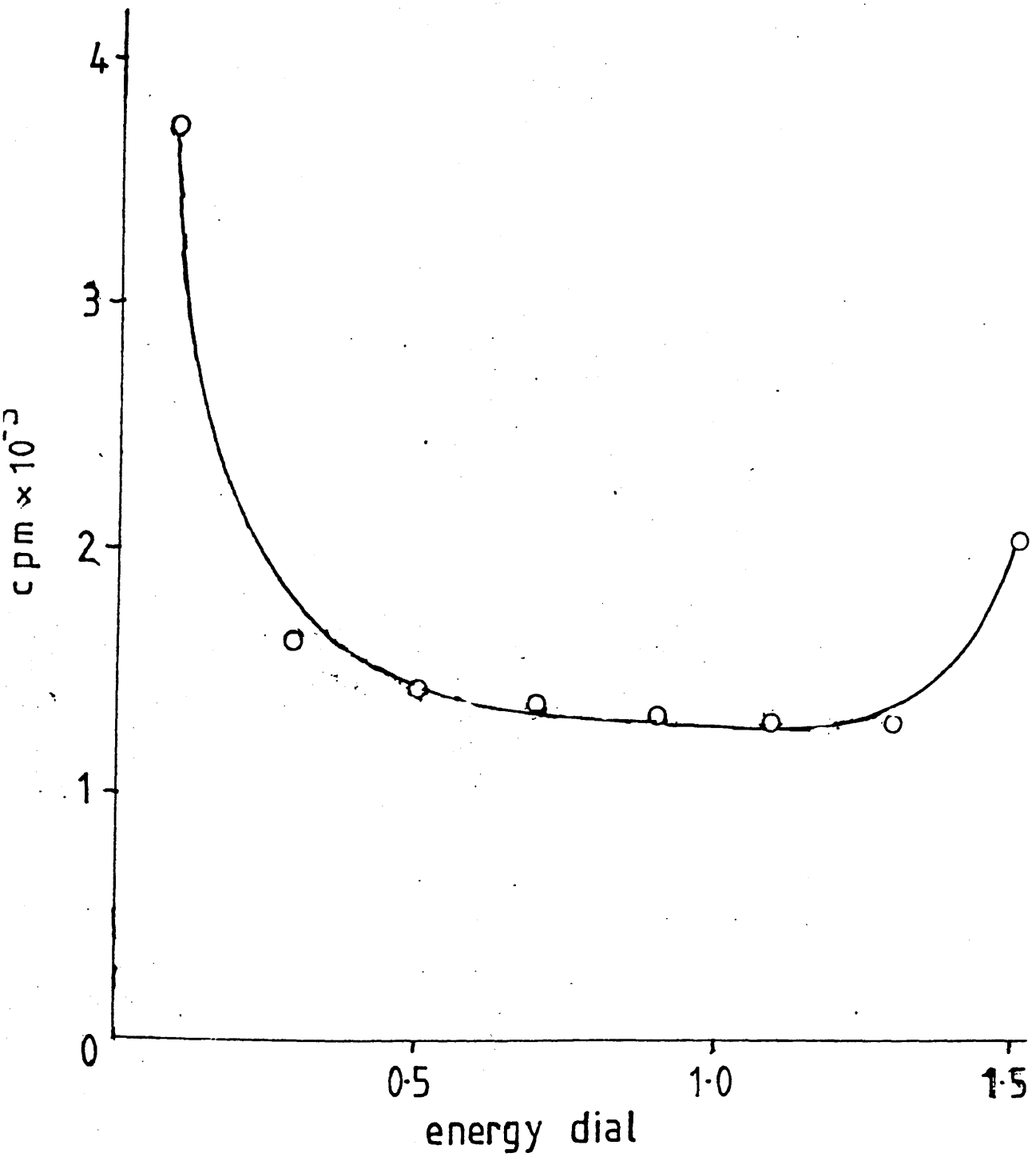


Figure 3.7.

Variation in observed counts for ^{60}Co external source with Discriminator Energy Dial Setting.

The proportionality of the counter's response to tritium was tested in two ways. Firstly, injections of various volumes of tritium were made and the count rates plotted against the volume of tritium. This is shown in figure 3.8.

In a separate experiment, a 500 μl aliquot of tritium of known specific activity was injected into the counting system. The tritium was then sequentially diluted with inactive hydrogen and 500 μl aliquots were injected after each dilution. Figure 3.9. shows the variation in measured activity with each dilution.

Although conditions were kept as uniform as possible in the radiotracer experiments, it was not practical to reproduce the exact specific activities of tritium from day to day; nor was the counter sensitivity precisely reproducible due to minute fluctuations in flow rates as a result of daily variation of ambient pressure and temperature. For this reason, daily calibrations of the counter were carried out.

3.8. The Proportional Counting of Tritium and Tritiated Hydrocarbons

During preliminary experiments involving the tritiation of catalysts and self-hydrogenation reactions on tritiated catalysts, there was obviously a malfunction affecting the efficiency of the counter in measuring the activity of tritium and tritiated products. This malfunction, which resulted in anomalous activities being measured, was found to have been remedied after the proportional counter had been stripped and reassembled, the anode wire replaced and retensioned, and a new supply of tritium introduced. Although the problem had been eradicated, it raised doubts concerning the performance of the counting system and therefore the properties of the system were further investigated.

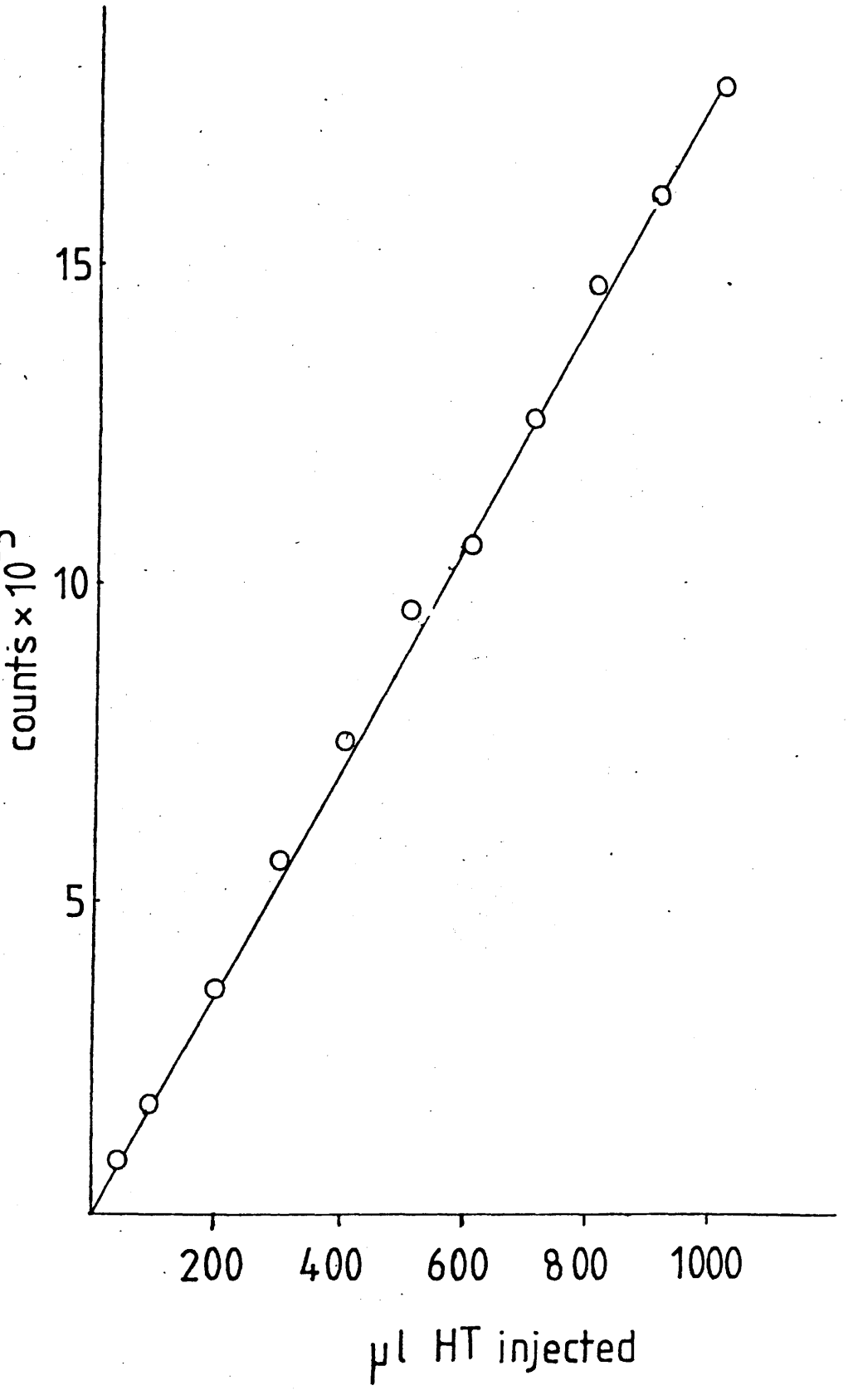


Figure 3.8.

Linearity of Counter Response (1).

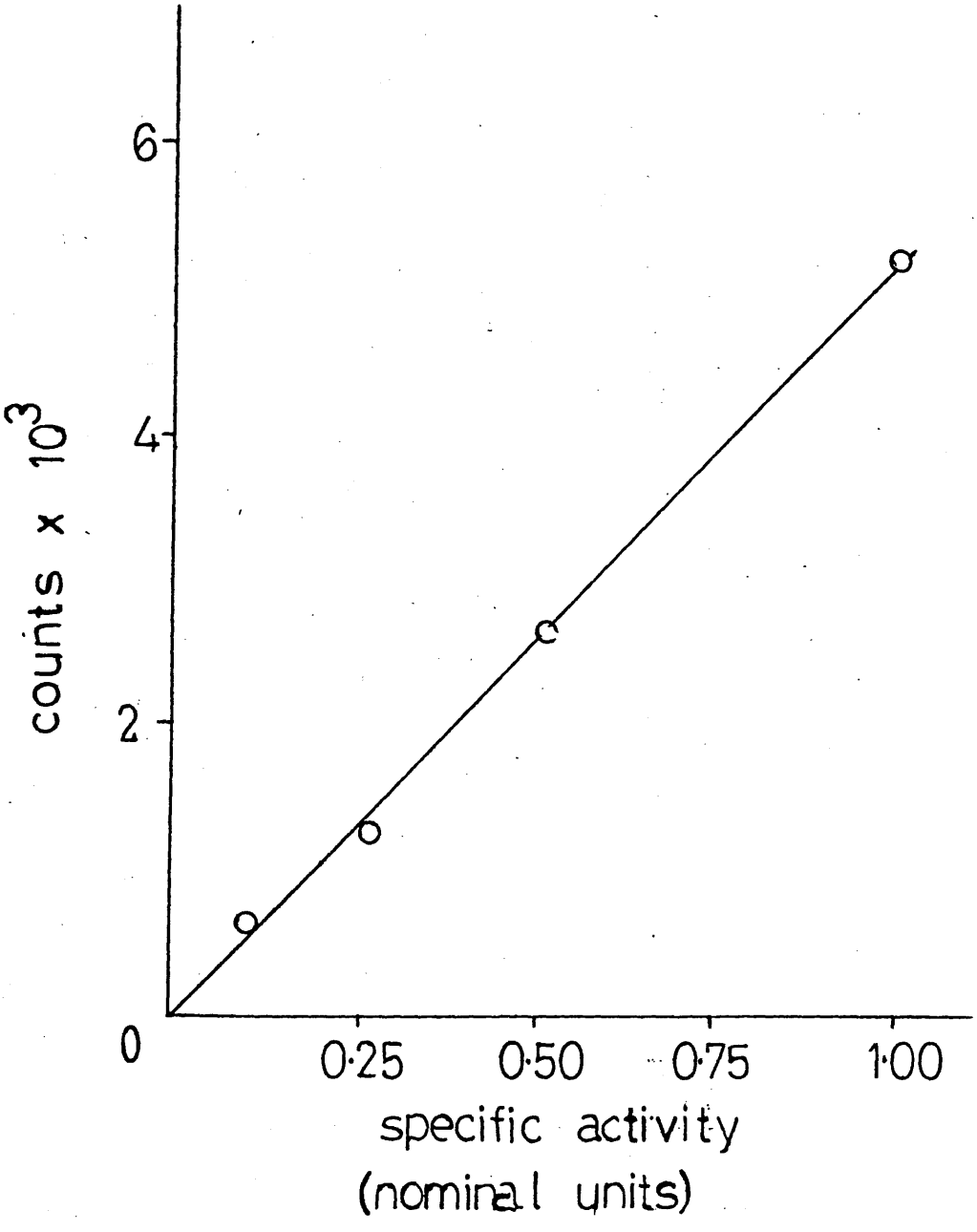


Figure 3.9.

Linearity of Counter Response (ii).

To ensure that the counter measured the activities of tritium and tritium-containing hydrocarbons equally well, several investigations were carried out.

In the first of these, the count rate observed when a measured activity of tritium was passed through the counter on its own, and the count rate observed when the same activity was passed through the counter in a pulse of hydrocarbon, were compared.

This was carried out by making up a mixture of tritium and hydrocarbon in a sample vessel. When this mixture was injected at the chromatograph reference port, IP2, the two components were separated by the chromatography column, and the tritium therefore entered the counter on its own. When the mixture was injected at injection port IP3, situated immediately after the chromatography column, the two components remained unseparated and entered the counter together. This was carried out for several hydrocarbon:tritium ratios, and for both butadiene and but-1-ene. It was found that the presence of butadiene and but-1-ene did not affect the count rate.

In a second investigation, the activities of tritiated acetylene and tritium gas were compared. Both cases were prepared from the same stock solution of tritiated water.

The tritiated acetylene was prepared by the reaction of tritiated water with calcium carbide. Both the calcium carbide and the tritiated acetylene were degassed before use.

The tritium gas was prepared by the reaction of phosphoric acid, produced *in situ* by the action of tritiated water on phosphorus pentoxide, with magnesium turnings. The reaction was carried out

in the vessel shown in figure 3.10. The vessel, containing P_2O_5, and magnesium, was attached to the vacuum line and evacuated. The vessel was then isolated, and tritiated water was injected through the septum cap.

Once the pressure of tritium inside the vessel had built up to slightly above atmospheric pressure, which was indicated by bubbles rising up through the mercury in the side-arm, an aliquot was removed in a gas-tight syringe and injected into the counter.

Although every effort was made to ensure that the tritium was at a high enough pressure before removing the sample, there was always some air contamination present, typically between 5 and 10% (estimated from the gas chromatograph peak), which reduced the number of counts observed. Once account had been taken of this, the observed activities of the tritium and the tritiated acetylene were in good agreement.

Therefore, it was considered that the proportional counter was responding to tritium and tritiated hydrocarbons equally, and that it was justified to assign tritium numbers to the various tritiated hydrocarbons produced in the self-hydrogenation reactions over tritiated catalysts.

3.9. Experimental Procedure

The experimental procedure was similar throughout the course of the present work.

a) A sample of catalyst, typically 0.50g, was placed into the glass catalyst chamber and a glass wool plug was placed over the catalyst to prevent small particles of catalyst being carried through the flow system on the carrier gas stream. The thermal well was then inserted and sealed in place with Apiczon W wax.

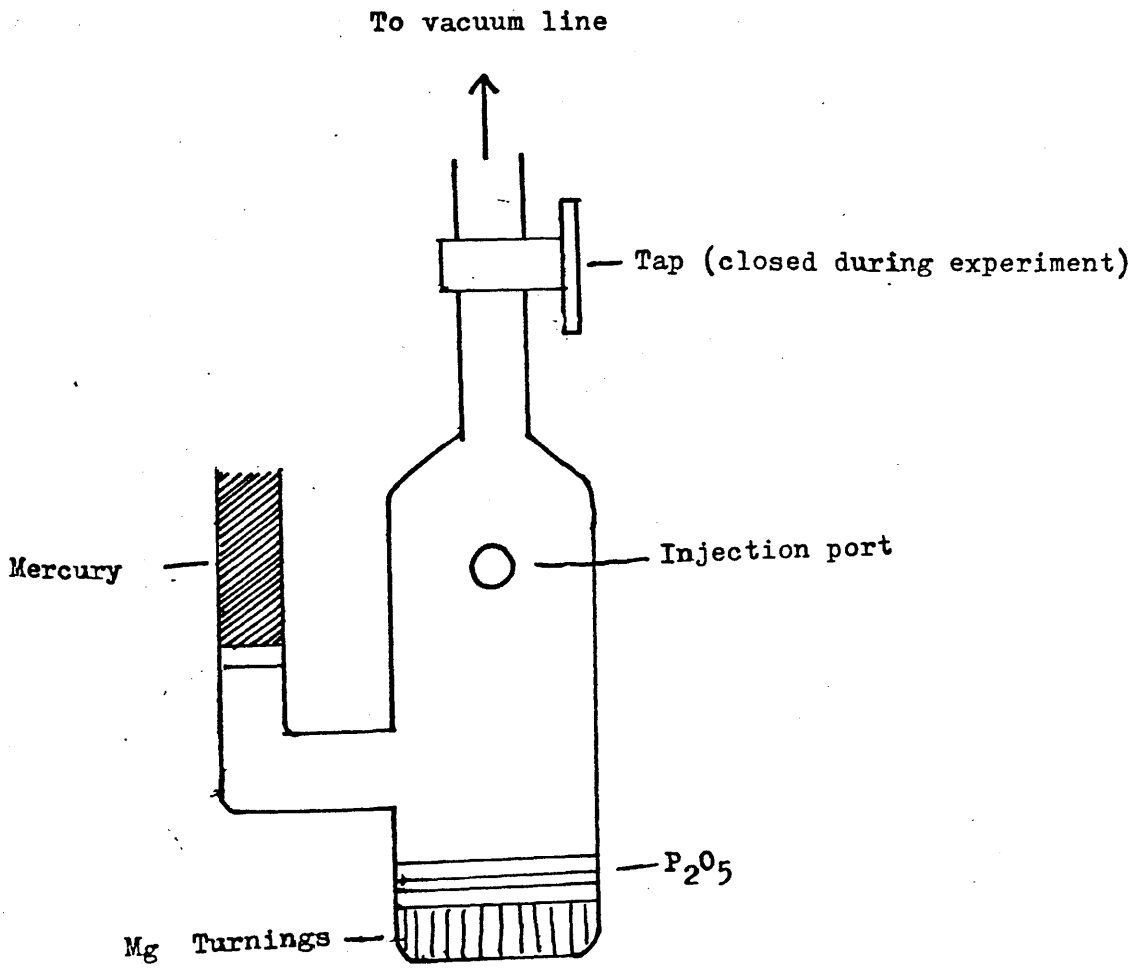


Figure 3.10

Reaction Vessel for Tritium Production

The septum caps in the injection ports were replaced, and the catalyst section was connected to the rest of the flow system. Helium was allowed to flow over the catalyst for some minutes to expel air, and then hydrogen was passed over the catalyst, the helium being diverted back to the sample arm of the katharometer via the by-pass circuit. The catalyst was then heated in flowing hydrogen to 633K and left at this temperature under flowing hydrogen (15ml min^{-1}) overnight.

When a catalyst was being regenerated, the same procedure was observed, the catalyst being cooled to room temperature under helium. The helium flow was then diverted and the injection ports dismantled so that the septa could be renewed.

When the reduction was complete, the hydrogen flow was stopped and the helium flow returned over the catalyst, being directed through the exhaust outlet for about a minute to expel gas phase hydrogen. The helium flow was then returned to the katharometer. The katharometer trace showed some deflection due to hydrogen in the helium flow, but the recorder returned to the baseline level within a few minutes, indicating that there was no hydrogen left in the flow system.

Once the katharometer trace had returned to the baseline level, replicate injections of the reactant were made at the reference port. Normally, three injections were sufficient to demonstrate the reproducibility of the chromatograph, and to provide a suitable calibration for the system. The catalyst was then cooled to the required reaction temperature, and adsorptions and reactions examined. If the experiment was long, calibration checks were carried out at intervals during the reaction.

b) In reactions involving the use of ^3H as a radiotracer, the reduction/regeneration of the catalyst and the calibration of the chromatograph were carried out as described above.

However, before the catalyst was cooled to the reaction temperature, the residual hydrogen on the catalyst from the reduction process was exchanged with 'tritium'.

A few torr of HT gas was admitted to one section of the secondary manifold and a sample vessel from a stock solution in a 2.5 litre storage vessel. The stock solution of HT, hereafter referred to as 'tritium', had been prepared by opening a 1 Ci ampoule of T_2 gas into the storage vessel and diluting it to approximately 720 torr with inactive hydrogen. These few torr of tritium in the manifold and the sample vessel were then further diluted to almost atmospheric pressure with inactive hydrogen passed through a palladium thimble purifier, and then contracted into the sample vessel. The sample vessel was then closed and the tritium allowed to warm again to room temperature. This provided a reservoir of tritium at super-atmospheric pressure suitable for transfer to the flow system. The normal specific activity of the tritium in the sample vessel was 1.5×10^5 - 2×10^5 counts per ml.

The tritiation of the catalyst was carried out by the flow exchange technique at 633K, the reduction temperature.

A series of injections of tritium were made at the reference port and the activity of each injection measured by the proportional counter. The counting mixture and the plateau had been determined whilst the hydrocarbon calibration was being carried out. It was generally found that a small proportion of the first injection of the

day was adsorbed onto the walls of the counter, as there was a marked increase in the background counting rate. After the counting system had been demonstrated to be reproducible, and the specific activity of the tritium had been calculated, injections of tritium were made over the catalyst. These were continued until the measured eluant activity became constant, a condition that was interpreted as indicating that saturation had been achieved. The tritiated catalyst was then cooled to the reaction temperature and reactions carried out with butadiene.

CHAPTER FOUR

THE INTERACTION OF BUTA-1,3-DIENE WITH 5% PLATINUM-SILICA CATALYSTS

4.1. Introduction

The investigations described in this chapter were carried out on regenerated 5% platinum-silica catalysts, that is, catalysts which had been used for reactions and then reactivated by treatment with hydrogen at 633K (section 3.8). Regenerated catalysts were used here and in the investigations reported in chapters 5 and 6, as it had been found quite early in the course of the present study that the regeneration process did not fully restore the activity of the catalyst to that of a fresh catalyst, that is, a catalyst which had been reduced directly from the supported salt. However, once a catalyst had been regenerated, subsequent regenerations gave a reproducible level of activity.

Some investigations of retention and self-hydrogenation on fresh 5% Pt/SiO_2 are described in chapter 7.

In the presentation of tables of results in this, and in subsequent chapters, the various C_4-hydrocarbons are denoted as n-b, 1-b, t-2-b, c-2-b, 1,3-b representing n-butane, but-1-ene, trans-but-2-ene, cis-but-2-ene and buta-1,3-diene respectively. Buta-1,3-diene is referred to hereafter as butadiene.

4.2. The Retention of Butadiene on 5% Pt/SiO_2 catalysts.

The extent to which butadiene was retained on 5% platinum-silica catalysts was investigated over the temperature range 323K to 523K.

A catalyst charge of 0.50g was used, the catalyst being regenerated after each series of reactions. Successive 500 μl aliquots of butadiene were injected on to the catalyst at each temperature and the amount of hydrocarbon eluted from the catalyst was measured in each case. The difference between the total eluted volume of hydrocarbon and the injected volume showed how much butadiene had been retained on the catalyst. The total amount of hydrocarbon eluted and the amount of butadiene retained by the catalyst are shown for a number of reactions at each temperature in table 4.1. Figure 4.1. illustrates the pattern of retention of each injection for the adsorption at 473K, which is typical of the behaviour observed.

Table 4.2. lists the percentage of butadiene retained following the initial pulse at each temperature, and table 4.3. shows the cumulative retention from a series of four successive adsorptions at each temperature. The initial retention is seen to be greatest at 523K, whilst the cumulative retention is greatest at 323K.

4.3. The Self-hydrogenation of Butadiene on 5% Pt/SiO_2 catalysts.

The self-hydrogenation of butadiene was studied by injecting 500 μl samples of butadiene into the helium carrier gas passing over the catalyst and determining the amounts of the various products in the reactor eluant. The self-hydrogenation was studied using regenerated catalyst samples (0.50g), at various temperatures between 323K and 523K.

The eluant was found to contain n-butane and the three n-butenes as well as unreacted butadiene. Some short-chain hydrocarbons were detected in the reactor eluant in the initial reaction at 523K.

TABLE 4.1.

Butadiene Retention on 0.50g Regenerated 5% Pt/SiO_2 (500 µl aliquots)

Temp (K)	Inj. No.	Hydrocarbon eluted (µl)	Buta-1,3-diene µl	Retained %age
323	1	226.1	273.9	54.78
	2	365.5	134.5	26.90
	3	361.7	138.3	27.66
	4	437.8	62.2	12.44
373	1	269.7	230.3	46.06
	2	406.0	94.0	18.80
	3	408.5	91.5	18.30
	4	408.1	91.9	18.38
	5	390.0	110.0	22.00
423	1	224.3	275.7	55.14
	2	346.7	153.3	30.66
	3	393.6	106.4	21.28
	4	422.5	77.5	15.50
473	1	239.5	260.5	47.90
	2	395.1	104.9	20.98
	3	403.2	96.8	19.36
	4	407.0	93.0	18.60
	5	404.9	95.1	19.02
523	1	187.0	313.0	62.60
	2	373.1	126.9	25.38
	3	398.1	101.9	20.38
	4	422.1	77.9	15.58

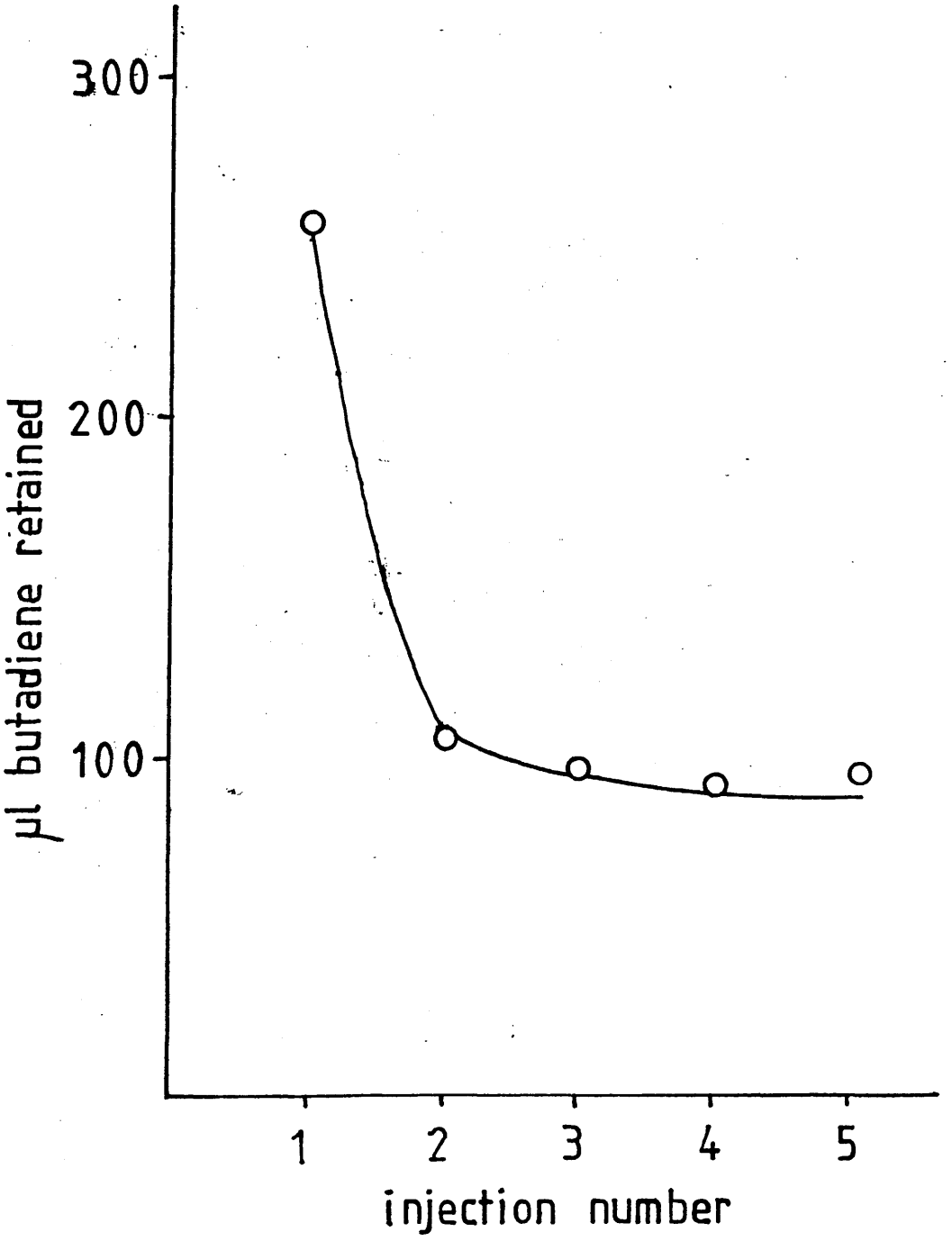


Figure 4.1.

The Retention of Butadiene on

Regenerated Platinum - Silica Catalysts

TABLE 4.2.

%age Butadiene retained after first 500 µl aliquot of Butadiene on 0.50g of 5% Pt/SiO_2.

Temp (K)	% Retention
323	54.78
373	46.06
423	55.14
473	47.90
523	62.60

TABLE 4.3.

Cumulative Retention from 4 x 500 µl aliquots of Butadiene on 0.50g of 5% Pt/SiO_2

Temp (K)	Cumulative µl	Retention molecules/g catalyst
323	882.8	4.747×10^{19}
373	507.7	2.730×10^{19}
423	612.9	3.296×10^{19}
473	555.2	2.986×10^{19}
523	619.7	3.333×10^{19}

Table 4.4. shows the complete analysis of the eluant from successive self-hydrogenation reactions at each temperature. The catalyst was regenerated overnight in flowing hydrogen at 633K after each series of reactions.

Self-hydrogenation occurs to the greatest extent with the first injection at each temperature, and it is in this first reaction that all or almost all of the n-butane formation is observed. Table 4.5. shows the variation in the extent of hydrogenation and the distribution of the three n-butenes with successive reactions at each temperature. The extent of hydrogenation is defined as

$$\text{Extent} = \frac{(2 \times \text{volume of n-butane}) + (\text{total volume of n-butene}) \times 100\%}{(\text{volume of butadiene injected})}$$

In this definition, total conversion of butadiene to n-butane would be denoted by an extent equal to 200%.

Figure 4.2. shows the decrease in the extent of hydrogenations in successive reactions. Figure 4.3. shows the relative distribution of the n-butenes at each temperature. But-1-ene is the most important of the n-butenes except in the first reaction at 523K. n-Butane production is greatest at 523K.

4.4. Tritiation of 5% Pt/SiO_2 catalysts

The exchange of hydrogen retained on the catalysts, following the reduction/regeneration process, with tritium was carried out by the flow exchange method (see chapter 3.8) at the reduction temperature. Successive aliquots, containing a measured activity of tritium, were injected over the catalyst and the eluted activity measured by proportional counting.

TABLE 4.4

The Self hydrogenation of Butadiene on 0.50g regenerated 5% Pt/SiO_2

Temp	Reaction No.	CH_4	C_2H_6/C_2H_4	C_3H_8	C_3H_6	n-b	1-b	t-2-b	c-2-b	1,3-b
323	1	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.0	224.6
	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	365.5
	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	361.7
	4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	437.8
373	1	0.0	0.0	0.0	0.0	T	27.8	9.0	1.7	231.2
	2	0.0	0.0	0.0	0.0	0.0	8.3	2.3	1.5	393.9
	3	0.0	0.0	0.0	0.0	0.0	5.3	1.4	0.96	400.8
	4	0.0	0.0	0.0	0.0	0.0	3.65	0.95	0.60	402.9
	5	0.0	0.0	0.0	0.0	0.0	2.7	0.84	0.53	385.9
	6	0.0	0.0	0.0	0.0	0.0	2.0	0.25	T	378.7
423	1	0.0	0.0	0.0	0.0	10.4	30.3	20.4	14.6	148.6
	2	0.0	0.0	0.0	0.0	0.0	17.6	9.6	6.9	312.6
	3	0.0	0.0	0.0	0.0	0.0	13.1	6.2	4.1	370.2
	4	0.0	0.0	0.0	0.0	0.0	5.6	3.1	2.5	411.3
	5*	0.0	0.0	0.0	0.0	0.0	3.0	2.0	0.8	279.7

TABLE 4.4 contd.

Temp K	Reaction No.	CH_4	C_2H_6/C_2H_4	C_3H_8	C_3H_6	n-b	1-b	t-2-b	c-2-b	1,3-b
473	1	0.0	0.0	0.0	0.0	16.1	36.1	24.5	20.6	142.2
	2	0.0	0.0	0.0	0.0	0.0	20.3	11.75	7.65	355.4
	3	0.0	0.0	0.0	0.0	0.0	10.3	6.9	4.75	381.2
	4	0.0	0.0	0.0	0.0	0.0	4.75	2.45	2.08	397.7
	5	0.0	0.0	0.0	0.0	0.0	2.77	1.3	0.74	400.1
	6	0.0	0.0	0.0	0.0	0.0	0.95	1.1	0.51	429.3
523	1	12.9	13.9	6.	2.9	96.5	15.6	32.2	20.8	4.9
	2	0.0	0.0	0.0	T	1.3	33.4	27.2	17.1	294.1
	3	0.0	0.0	0.0	0.0	T	18.8	13.5	9.0	356.8
	4	0.0	0.0	0.0	0.0	0.0	13.8	9.15	6.06	393.1

*: Less than 500 µl injected.

T: Trace amount observed.

TABLE 4.5.

The variation of Butene Distribution and extent of Hydrogenation with successive reactions

Temp K	Reaction No.	Extent (%)	% 1-b	% t-2-b	% c-2-b	$\frac{1\text{-b}}{2\text{-b}}$	$\frac{t}{c}$
323	1	0.6	0.0	0.0	0.0	-	-
	2	0.00	0.0	0.0	0.0	-	-
	3	0.00	0.0	0.0	0.0	-	-
	4	0.00	0.0	0.0	0.0	-	-
373	1	7.70	72.21	23.38	4.41	2.598	5.302
	2	2.42	68.60	19.06	12.40	2.185	1.532
	3	1.53	69.19	18.28	12.53	2.246	1.459
	4	1.04	70.19	18.27	11.54	2.354	1.583
	5	0.81	66.34	20.64	13.02	1.971	1.585
	6	0.45	-	-	-	-	-
423	1	17.22	46.40	31.24	22.36	0.866	1.397
	2	6.82	51.61	28.15	20.24	1.067	1.391
	3	4.68	55.98	26.50	17.52	1.272	1.512
	4	2.24	50.00	27.68	22.32	1.000	1.240
	5	1.16	51.72	34.48	13.80	1.071	2.500
473	1	22.68	44.46	30.17	25.37	0.800	1.189
	2	7.94	51.13	29.60	19.27	1.046	1.536
	3	4.39	46.92	31.44	21.64	0.884	1.453
	4	1.86	51.19	26.40	22.41	1.049	1.178
	5	0.96	57.59	27.03	15.38	1.358	1.757
	6	0.51	37.11	42.97	19.92	0.590	2.157
523	1	52.32	22.74	46.94	30.32	0.294	1.548
	2	16.06	42.99	35.00	22.01	0.754	1.591
	3	8.26	45.52	32.69	21.79	0.825	1.500
	4	5.80	47.57	31.54	20.89	0.907	1.510

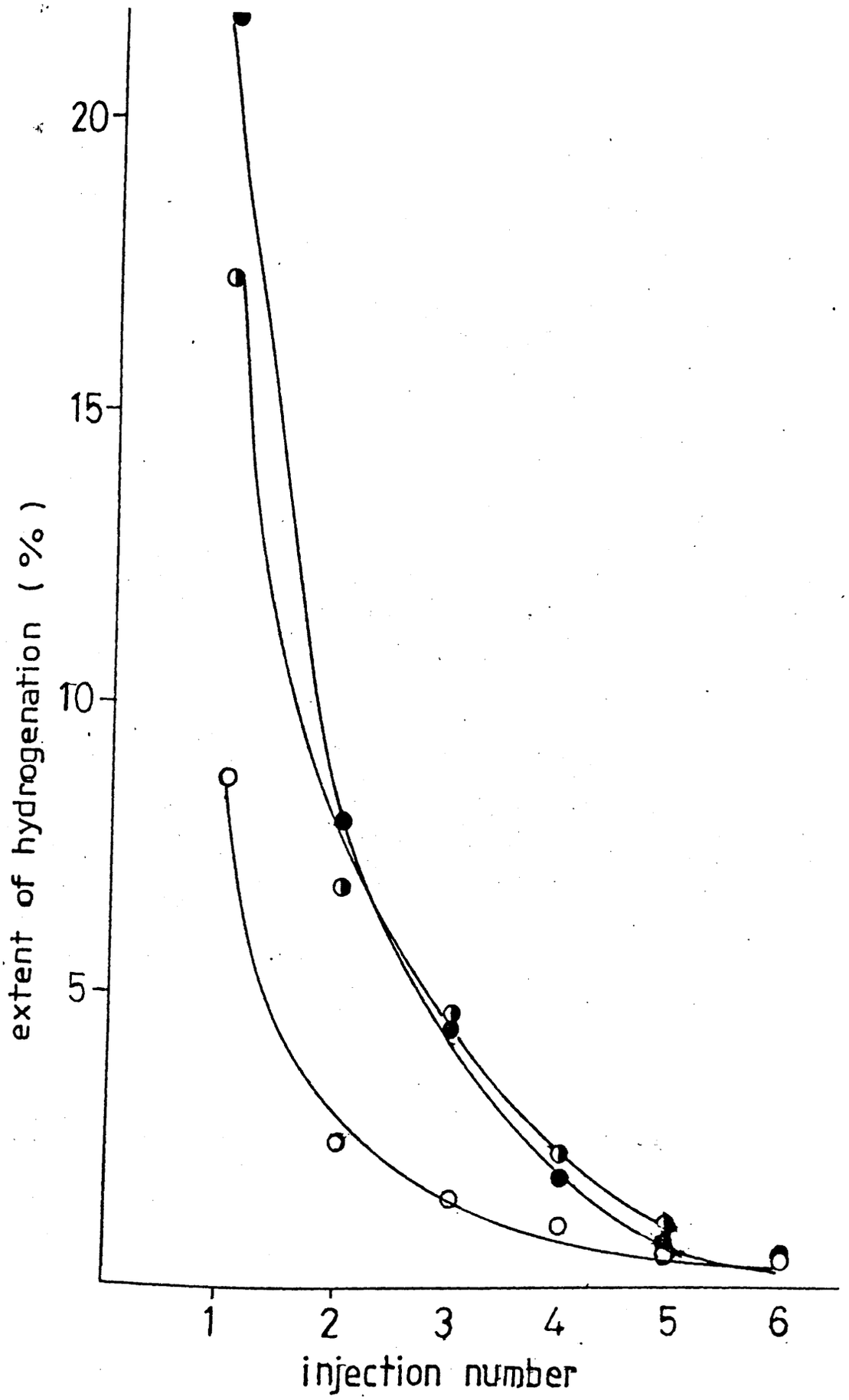


Figure 4.2.

Variation of Extent of Hydrogenation with Reaction Number at Various Temperature (○ = 373K, ◑ = 423K, ● = 473K).

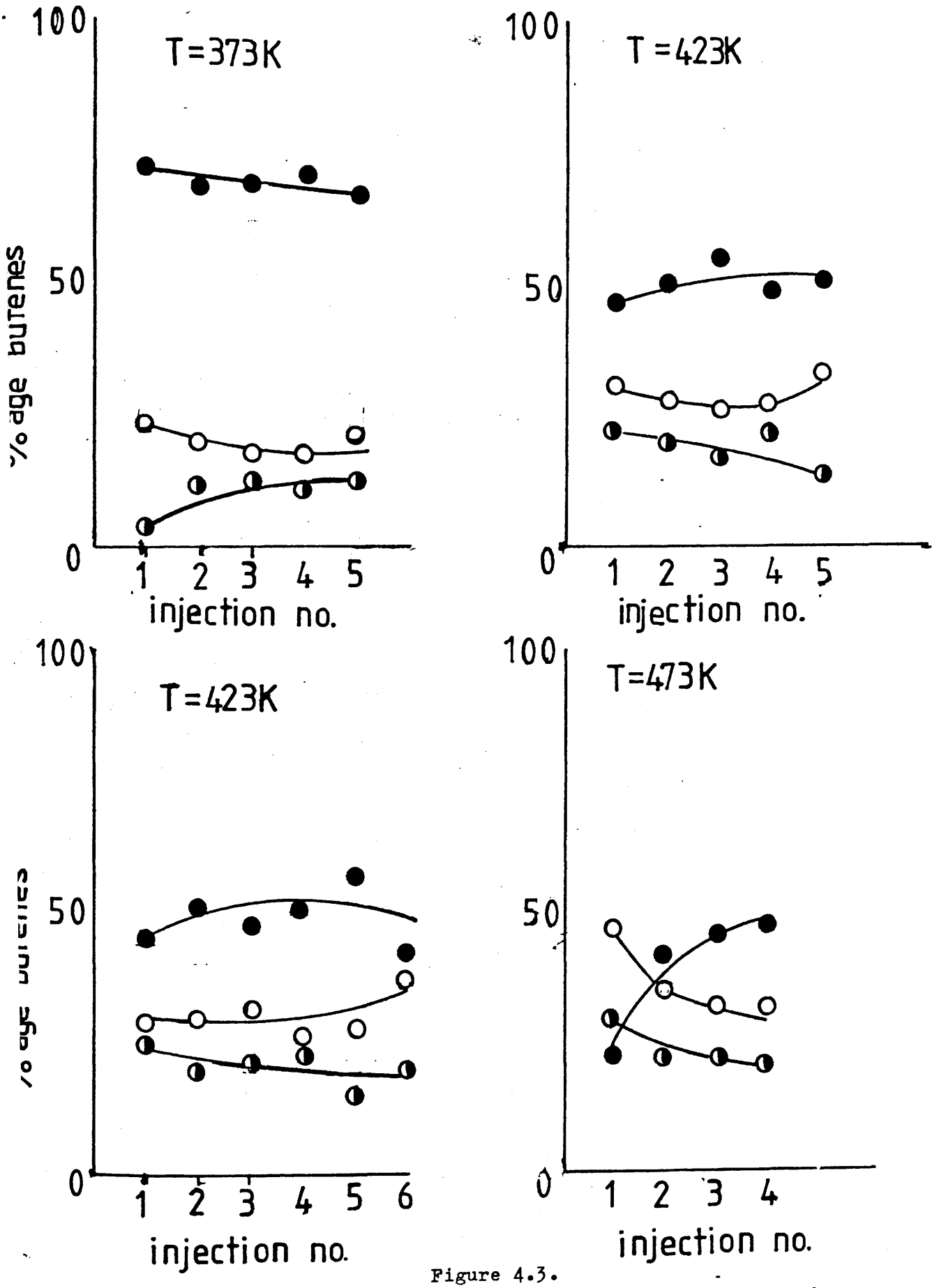


Figure 4.3.

Butene Distribution as a Function of Injection Number

(● = 1-b, ○ = t-2-b, ◑ = c-2-b.)

Figure 4.4 shows that the eluted activity, when plotted against aliquot number, rises steeply in the initial stages, before reaching an almost constant level after about 6mls of tritium have been passed over the catalyst. Figure 4.5 shows the result of an investigation of this initial steeply rising region using smaller 0.5ml aliquots. This shows that the linear region is actually reached after the first 3.5ml of tritium has been injected over the catalyst.

The amount of tritium exchanged in a typical reaction with successive 1ml aliquots of tritium is shown in table 4.6 and in figure 4.6.

4.5. Reaction of Butadiene on Tritiated 5% Pt/SiO_2 Catalysts

In order to investigate the possible role of any hydrogen retained on the catalyst following the reduction/regeneration process or present as surface hydroxyl groups on the support (50) in the reactions discussed in section 4.3, the hydrogen was replaced by tritium using the flow exchange technique.

The procedure was as described in section 4.4, tritium exchange being continued until constant activity had been reproducibly demonstrated in the reactor eluant. Normally a total of 10 - 12ml of tritium was passed over the catalysts. Constant eluant activity was assumed to indicate that tritium exchange was complete.

The catalyst was then cooled to the reaction temperature and reactions were then carried out by injecting 500 μl samples of butadiene into the helium carrier gas flowing over the catalyst. The reactor eluant was analysed by gas chromatography, and the activity of the separated reaction products was measured by proportional counting.

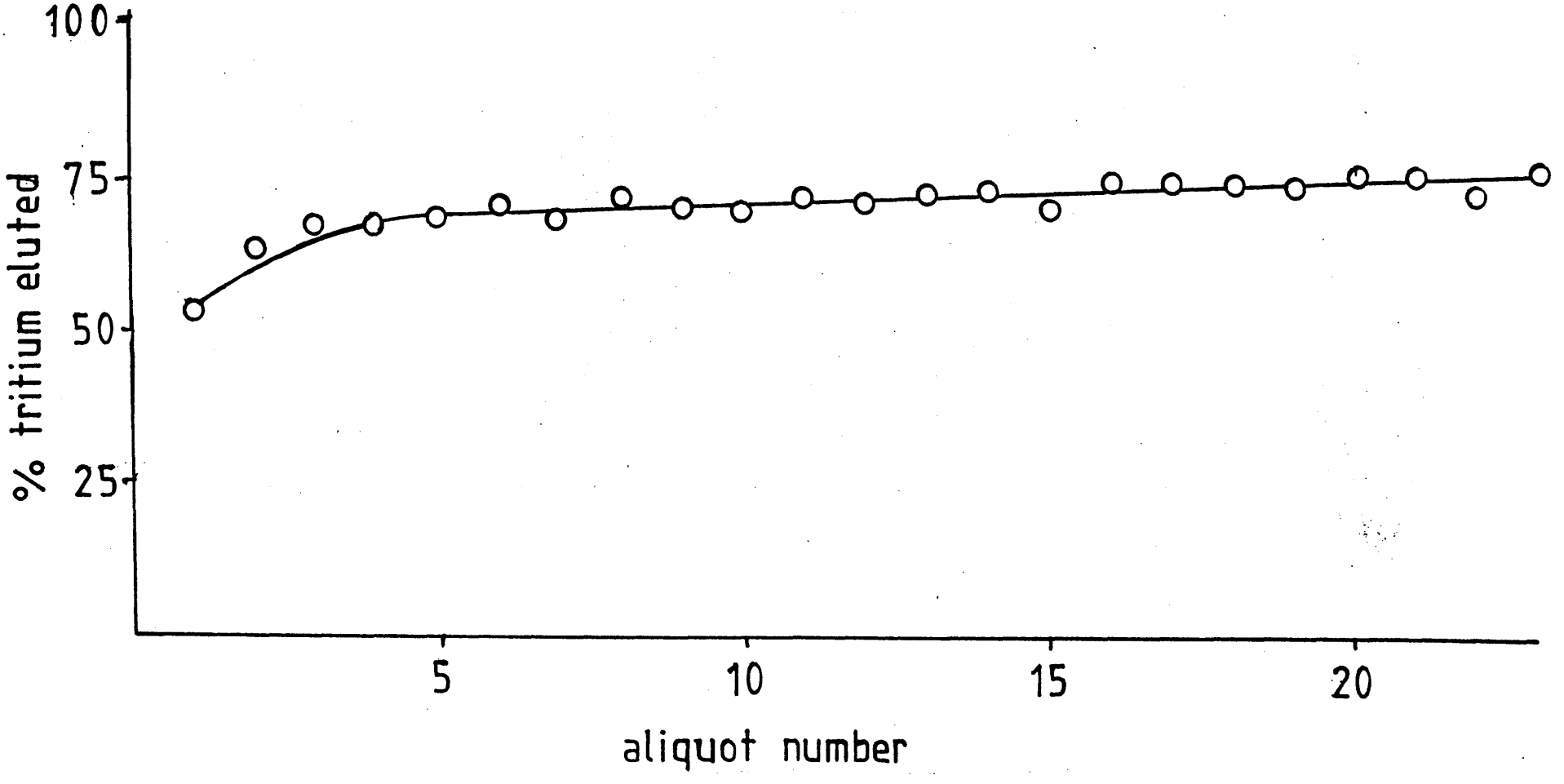


Figure 4.4.

Tritiation of 500mg 5% Pt/SiO_2 Catalyst

By 1000µl Aliquots.

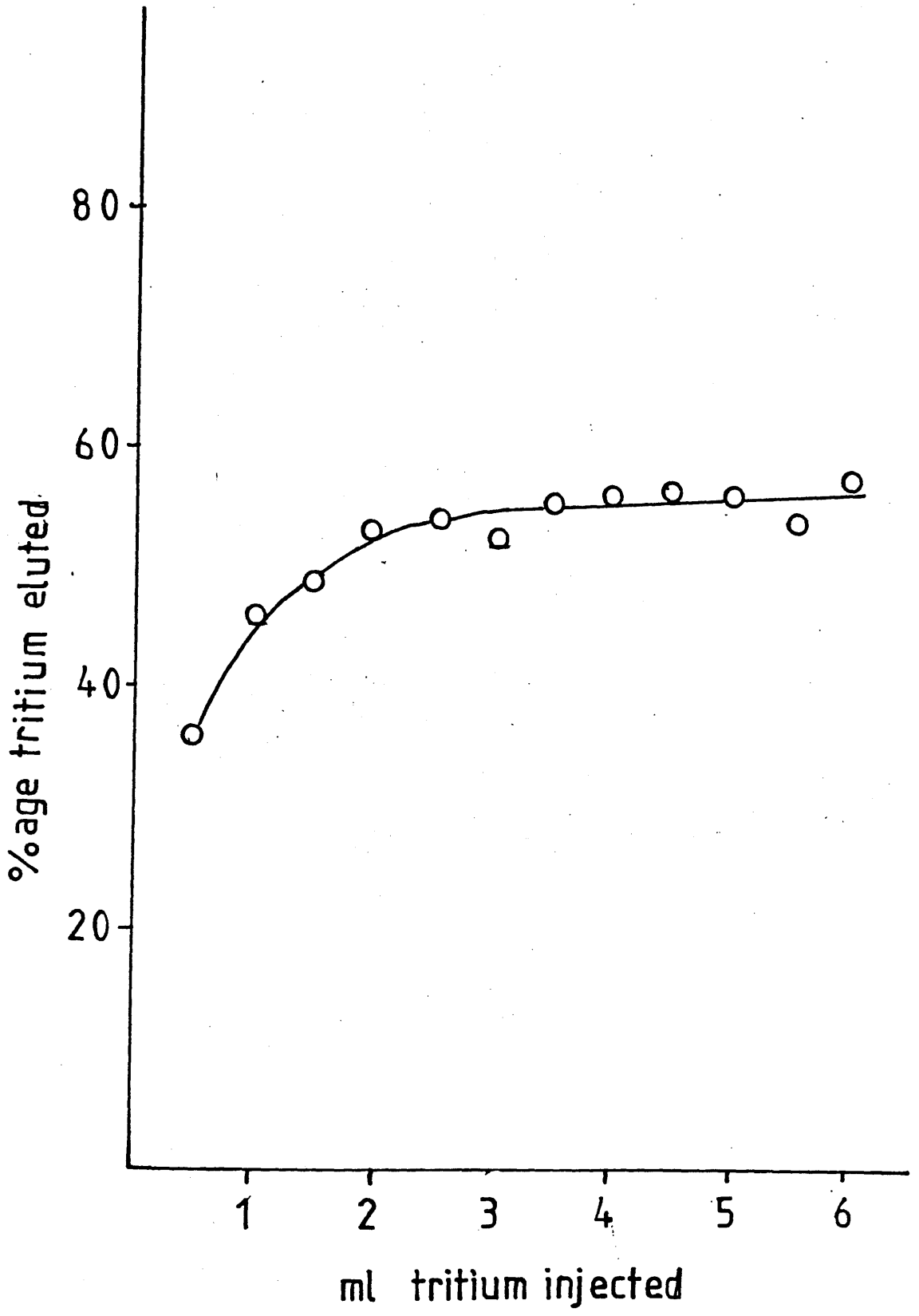


Figure 4.5.

Tritiation of 0.50g Pt/SiO_2

by 500 μl Aliquots.

TABLE 4.6.

The exchange of successive 1ml aliquots of Tritium on a 5% Pt/SiO_2 catalyst.

Injection No.	Tritium Exchanged (μl)	Cumulative μl	Exchange atoms x 10^{-19}
1	447.1	447.1	2.405
2	352.9	800.0	4.302
3	328.6	1128.6	6.850
4	316.7	1445.3	7.772
5	312.6	1757.9	9.453
6	290.2	2048.1	11.014
7	312.4	2360.5	12.694
8	289.3	2649.8	14.250
9	295.8	2945.6	15.841
10	304.6	3250.2	17.478
11	279.4	3529.6	18.981
12	290.1	3819.7	20.541
13	278.6	4098.3	22.039
14	264.6	4369.	23.462
15	292.5	4662.5	25.073
16	261.7	4924.1	26.480
17	252.1	5176.2	27.836
18	257.7	5433.9	29.222
19	264.1	5698.0	30.642
20	252.9	5950.9	32.002
21	251.3	6202.2	33.353
22	275.6	6477.8	34.835
23	246.4	6724.2	36.161

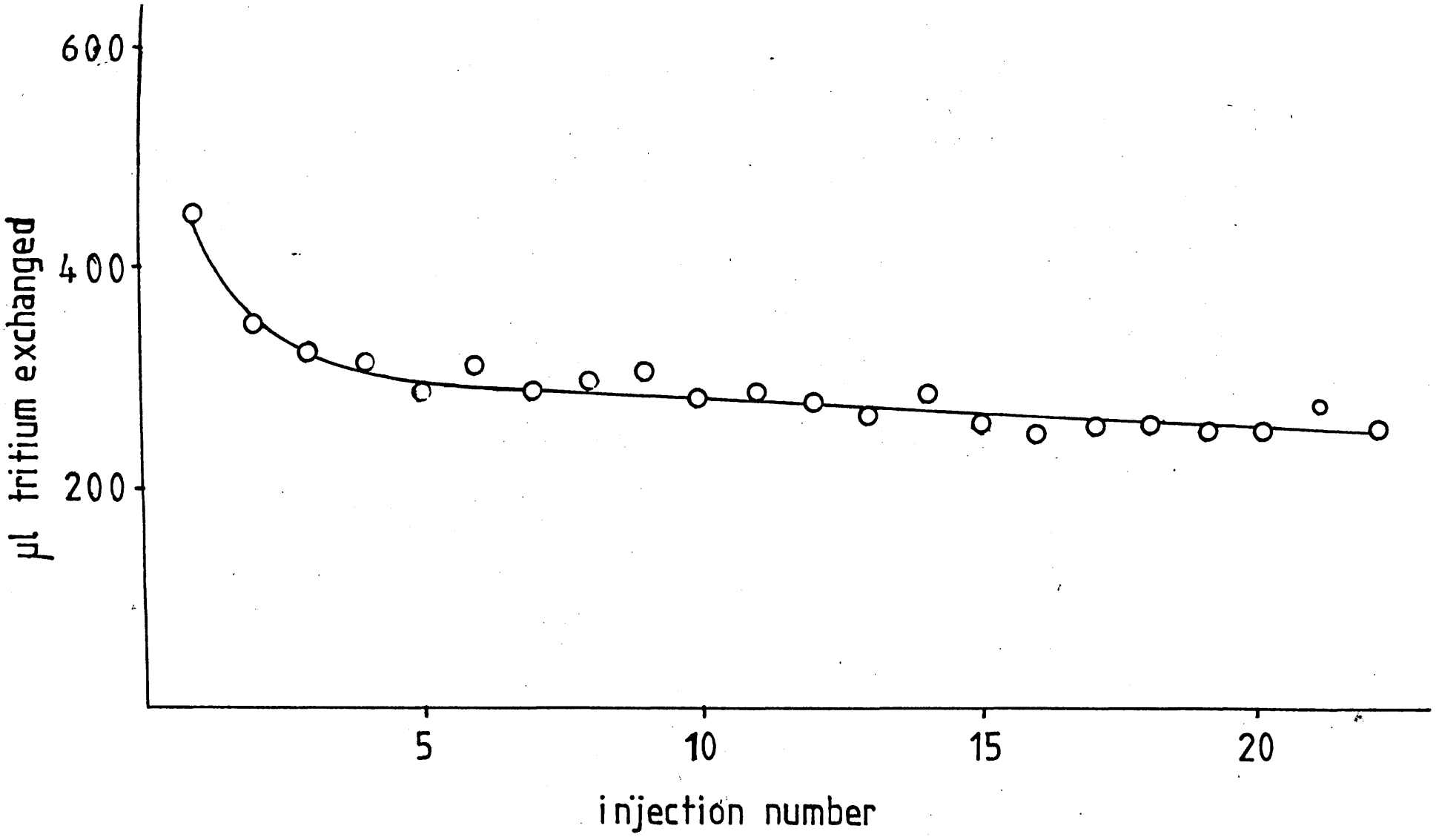


Figure 4.6.

Exchange of Tritium on 5% Pt/SiO_2

The specific activity of the individual products was calculated by dividing the measured activity of the products by its volume. This was then converted to a 'Tritium Number' by, firstly, dividing the specific activity of the hydrocarbon by the specific activity of the tritium used in the tritium exchange process, and then, as the tritium contained two ^{3}H atoms per molecule, multiplying the quotient by two, to give the number of tritium atoms present in the hydrocarbon.

Where the measured activity was less than the expected error in the background count(the square root of the expected background count for the counting period), the activity was taken as zero in the calculation of specific activities and tritium numbers.

Table 4.7 shows the product distribution and the radioactive content of the products for several reactions at temperatures between 323K and 523K.

TABLE 4.7.

Self-hydrogenation of Butadiene on Tritiated 5% Pt/SiO_2

Temp K	Reaction No.	n-but	n-but T.No.	1-but	1-but T.No.	t-2-but	t-2-but T.No.	c-2-but	c-2-but T.No.	1,3-but	1,3-but T.No.
323	1	1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	224.6	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	365.5	0.0
	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	361.7	0.0
	4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	437.8	0.0
373	1	T	-	27.8	0.260	9.0	0.354	1.7	1.212	231.2	0.0198
	2	0.0	0.0	8.3	0.394	2.3	0.594	1.5	1.246	393.9	0.0134
	3	0.0	0.0	5.3	0.624	1.4	1.058	0.96	1.706	400.8	0.0128
	4	0.0	0.0	3.65	0.472	0.95	1.034	0.60	1.486	402.9	0.0088
	5	0.0	0.0	2.7	0.488	0.84	0.780	0.53	0.596	385.9	0.0046
	6	0.0	0.0	2.0	0.280	0.25	0.680	T	-	378.7	0.0038
423	1	10.4	0.752	30.3	0.430	20.4	0.596	14.6	0.582	148.6	0.0514
	2	0.0	0.0	17.6	0.598	9.6	0.824	6.9	0.734	312.6	0.0524
	3	0.0	0.0	13.1	0.738	6.2	0.956	4.1	*	370.2	0.0474
	5	0.0	0.0	5.6	0.732	3.1	1.134	2.5	0.920	411.3	0.0200
	6			3.0	0.414	2.0	0.636	0.8	0.0	**	**

TABLE 4.7. contd.

Temp K	Reaction No.	n-but l	n-but T.No.	1-but l	1-but T.No.	t-2-but l	t-2-but T.No.	c-2-but l	c-2-but T.No.	1,3-but l	1,3-but T.No.
473	1	16.1	0.978	36.1	0.224	24.5	0.360	20.6	0.330	142.2	0.0388
	2	0.0.	0.0	20.3	0.380	11.75	0.498	7.65	0.532	355.4	0.0226
	3	0.0	0.0	10.34	0.304	6.9	0.570	4.75	0.708	381.2	0.0208
	4	0.0	0.0	4.75	0.404	2.45	0.542	2.08	1.032	397.7	0.0154
	5	0.0	0.0	2.77	0.360	1.3	0.0	0.74	*	400.1	0.0100
	6	0.0	0.0	0.95	*	1.1	0.0	0.51	0.0	429.3	0.0040
523	1	96.5	0.494	15.6	0.158	32.2	0.202	20.8	0.422	4.9	0.00
	2	1.3	1.330	33.4	0.270	27.2	0.336	17.1	0.450	294.1	0.0350
	3	T	-	18.8	0.248	13.5	0.310	9.0	0.308	356.8	0.0312
	4	0.0	0.0	13.8	0.186	9.15	0.160	6.06	0.0	393.1	0.0184

* Counts less than expected error levels.
** Not measured.

CHAPTER FIVE

THE INTERACTION OF BUTADIENE WITH 5% PALLADIUM - SILICA CATALYSTS

5.1. Introduction

A series of investigations, similar to those described in chapter 4 for the 5% platinum-silica catalyst, was carried out using a 5% palladium-silica catalyst.

It was found that the palladium catalyst was much less dense than the platinum catalyst and, in consequence, the catalyst bed was approximately twice as long as was the case with the platinum catalyst. This had the effect of reducing the maximum operating flow rate of the helium carrier gas from 60ml min^{-1} to approximately 40ml min^{-1} which, in turn, had an adverse effect on the chromatographic resolution, particularly of the but-2-enes. It was, therefore, decided to reduce the catalyst charge to 0.25g and the reactant dose to 250 μl. This ensured that the same reactant to catalyst ratio was maintained, and allowed the carrier gas flow rate to be restored to 60ml min^{-1}.

5.2. The Retention of Butadiene on 5% Pd/SiO_2 catalysts.

A study was made of the amount of butadiene retained on a 0.25g sample of the 5% Pd/SiO_2 catalyst over the temperature range 323K to 523K. Successive 250 μl aliquots of butadiene were injected on to the catalyst at each temperature, and the amount of butadiene retained following each injection was calculated by measuring the volume of hydrocarbon eluted by gas chromatography. The same catalyst sample was used in each series of reactions, the catalyst being regenerated overnight in flowing hydrogen at 633K after each series of reactions.

Table 5.1 shows the volume of hydrocarbon eluted and the volume of butadiene retained on each injection for each series of experiments. The amount of butadiene retained is also shown as a percentage of the injected aliquot. Retention is generally seen to decline to an approximately steady value at each temperature. Table 5.2 compares the initial percentage of butadiene retained at each temperature. Retention is always seen to be greatest following the first injection, and is seen to be greatest at 473K.

The cumulative retentions for five successive injections of butadiene are shown in Table 5.3. Cumulative retention is greatest at 473K and lowest at 323K. Figure 5.1 shows the variation of the percentage retention of butadiene, following the first reaction, with temperature, and figure 5.2 shows the variation of the cumulative retention with temperature.

5.3. The Self-hydrogenation of Butadiene on 5% Pd/SiO_2.

The interaction of butadiene with a 5% Pd/SiO_2 catalyst in the absence of added molecular hydrogen was studied over the temperature range 323K to 523K.

Successive 250 μl aliquots of butadiene were injected over a 0.25g sample of regenerated 5% Pd/SiO_2 catalyst and the eluant was analysed by gas chromatography. The catalyst was regenerated between each set of reactions.

A complete analysis of the reaction eluants at each temperature is shown in table 5.4. The conversion is low at all temperatures and the accuracy of the smaller volumes quoted is thus impaired. A letter

TABLE 5.1.

The Retention of Butadiene on 0.25g of 5% Pd/SiO_2

Temp K.	Injn. No.	Hydrocarbon eluted (μl)	Butadiene μl	Retained %age
323	1	199.5	50.1	20.44
	2	220.0	30.0	12.00
	3	224.4	25.6	10.24
	4	230.9	19.1	7.64
	5	231.1	19.9	7.96
	6	-	-	-
373	1	192.2	57.8	23.12
	2	228.0	22.0	8.80
	3	197.8	52.2	20.88
	4	198.0	52.0	20.80
	5	204.9	45.1	18.04
	6	199.1	50.9	20.36
423	1	174.4	75.6	30.23
	2	221.1	28.9	11.56
	3	220.6	29.4	11.76
	4	231.8	18.2	7.28
	5	220.5	29.5	11.80
	6	218.6	31.4	12.56
473	1	165.3	84.7	33.88
	2	197.9	52.1	20.84
	3	203.6	46.4	18.56
	4	217.3	32.7	13.08
	5	207.8	42.2	16.88
	6	203.1	46.9	18.76
523	1	177.7	72.3	28.92
	2	222.2	27.8	11.12
	3	198.2	51.8	20.72
	4	200.5	49.5	19.80
	5	206.0	44.0	17.60
	6	207.6	42.4	16.96

TABLE 5.2.

%age Retention of First 250 μl Aliquot of Butadiene on 0.25g regenerated 5% Pd/SiO_2.

Temp (K)	%age Retention
323	20.04
373	23.12
423	30.23
473	33.88
523	28.92

TABLE 5.3

Cumulative Retention from 4 x 250 μl Aliquots of Butadiene on 0.25g of Regenerated 5% Pd/SiO_2.

Temp (K)	Cumulative μl	Retention molecules/g catalyst
323	124.8	1.342×10^{19}
373	184.0	1.979×10^{19}
423	152.1	1.636×10^{19}
473	215.9	2.322×10^{19}
523	201.4	2.1661×10^{19}

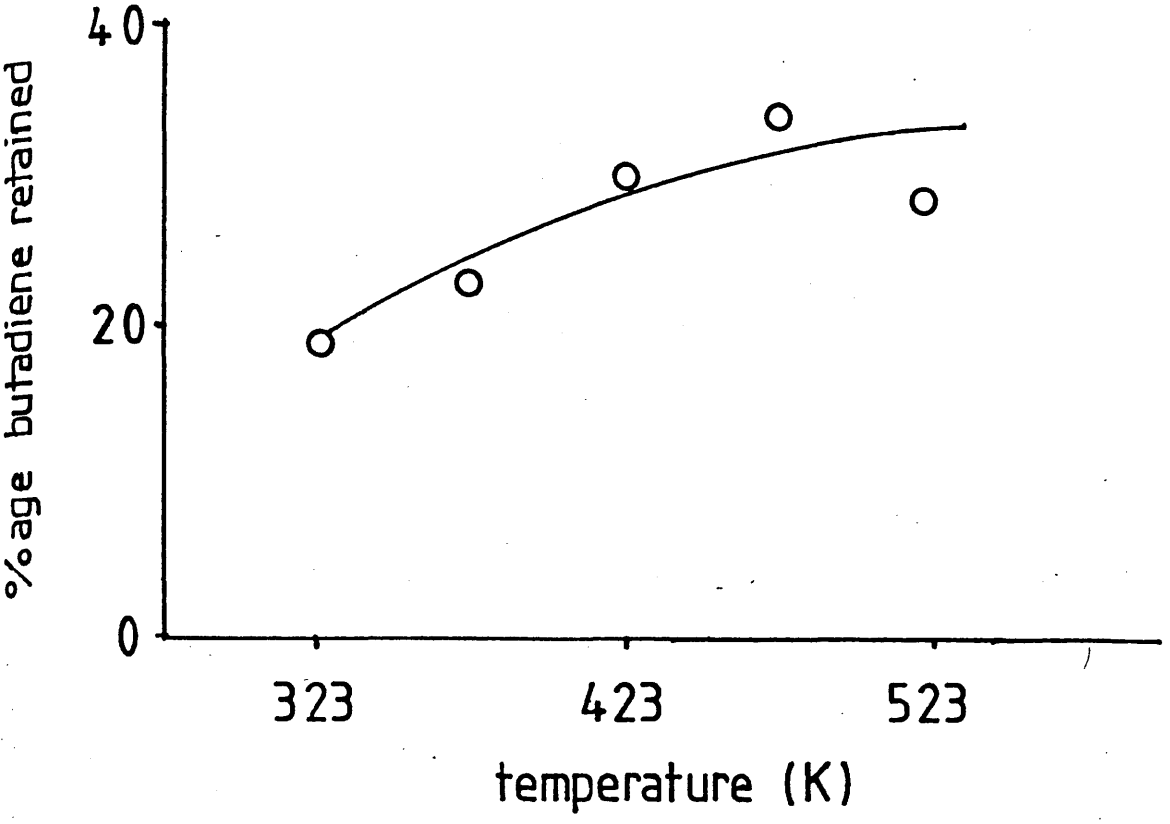


Figure 5.1.

Initial Retention of Butadiene on 5% Pd/SiO_2.

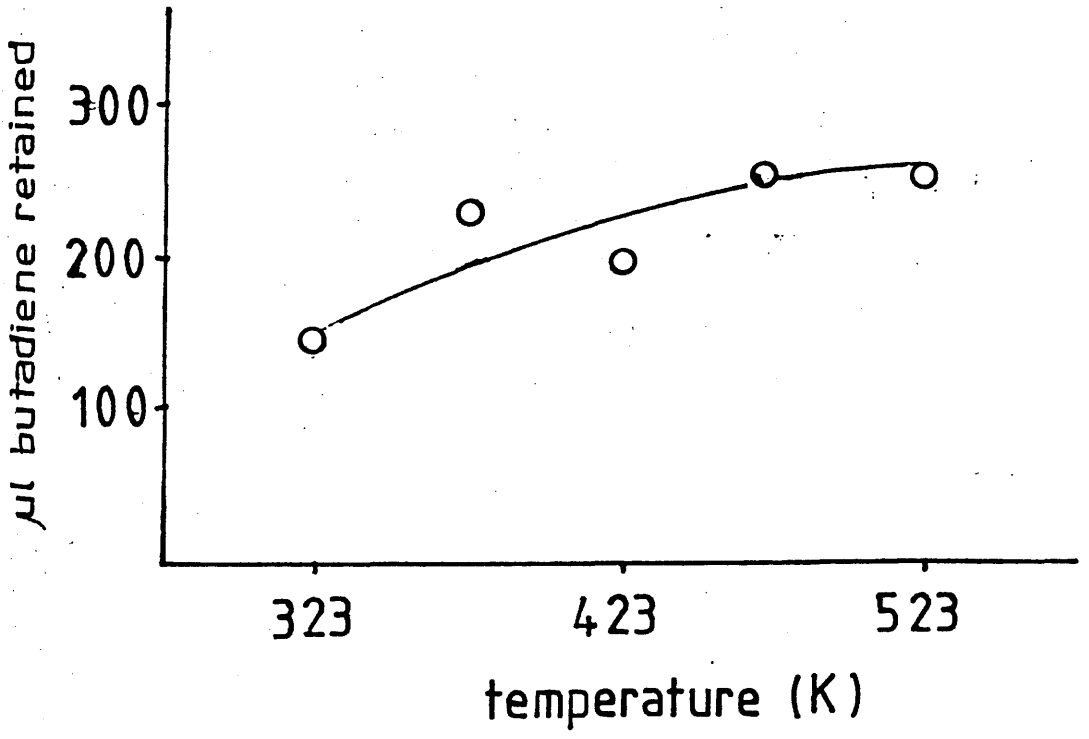


Figure 5.2.

Cumulative Retention of Four Butadiene Aliquots on 5% Pd/SiO_2.

'T' in table 5.4 indicates that a trace amount of a hydrocarbon was detected by gas chromatography, but the peak was too small and/or diffuse for its area to be measured with any degree of accuracy. Normally, this would correspond to less than 0.5 μl.

Table 5.5 analyses the information in table 5.4., and presents information on the extent of hydrogenation, the selectivity, and the product butene distribution. The extent of hydrogenation is seen to increase with temperature, but also to decrease very rapidly with reaction number. The extent of the reaction is small, and only at 523K does hydrogenation continue after the third injection. Butane is only observed on the first reaction at each temperature.

But-1-ene is the principal product at low temperatures, but at 423K but-1-ene and trans-but-2-ene yields are approximately equal, trans-but-2-ene being the major product above 423K. The trans:cis ratio is generally about two throughout a series of reactions at each temperature. Only at 323K and 373K is but-1-ene yield greater than the combined but-2-ene yields. The butene distribution for the reaction at 523K is shown in figure 5.3.

5.4. Tritiation of 5% Pd/SiO_2 catalysts.

The hydrogen retained on the catalyst following the regeneration process was exchanged with tritium by the flow exchange method.

A constant eluant activity was quickly reached after two or three 1ml injections of tritium. The amount of tritium eluted after each of a series of tritium injections over the catalyst at 360°C is shown in figure 5.4.

TABLE 5.4.

The Self-hydrogenation of Butadiene on 5% Pd/SiO_2.

Temp (K)	Reaction No.	Volume (μl) n-but	1-but	t-2-but	c-2-but	1,3-but
323	1	0.0	0.4	0.1	T	199.0
	2	0.0	T	T	0.0	220.0
	3	0.0	0.0	0.0	0.0	224.4
	4	0.0	0.0	0.0	0.0	230.9
	5	0.0	0.0	0.0	0.0	231.1
373	1	0.0	2.37	1.52	0.47	187.8
	2	0.0	0.12	T	T	227.8
	3	0.0	T	0.0	0.0	197.8
	4	0.0	0.0	0.0	0.0	198.0
	5	0.0	0.0	0.0	0.0	204.9
	6	0.0	0.0	0.0	0.0	199.1
423	1	0.2	6.4	5.4	2.7	168.8
	2	0.0	1.15	1.56	0.75	199.1
	3	0.0	0.53	0.6	T	212.8
	4	0.0	T	T	T	231.8
	5	0.0	0.0	0.0	0.0	220.5
	6	0.0	0.0	0.0	0.0	218.6
473	1	0.15	3.34	8.44	3.45	155.5
	2	0.0	1.34	3.77	1.83	191.0
	3	0.0	T	0.72	0.25	202.6
	4	0.0	0.0	0.0	0.0	217.3
	5	0.0	0.0	0.0	0.0	207.8
	6	0.0	0.0	0.0	0.0	203.1
523	1	5.7	5.3	12.8	6.8	147.1
	2	0.0	2.04	4.7	2.0	213.5
	3	0.0	0.96	2.18	0.93	194.1
	4	0.0	1.06	3.17	0.96	195.3
	5	0.0	0.96	1.84	0.52	202.7
	6	0.0	0.79	1.57	0.41	204.8

TABLE 5.5.

The variation of the butene distribution and the extent of self-hydrogenation in successive reactions

Temp.	Reaction	Extent	Butene Distribution(%age)			1-b / 2-b	t / c
			1-but	t-2-but	c-2-but		
323	1	0.2	80.0	20.0	-	4.00	-
	2	0.0	-	-	0.0	-	-
	3	0.0	0.0	0.0	0.0	-	-
	4	0.0	0.0	0.0	0.0	-	-
	5	0.0	0.0	0.0	0.0	-	-
373	1	1.7	54.35	34.86	10.78	1.191	3.23
	2	0.05	100.0	-	-	-	-
	3	0.0	0.0	0.0	0.0	-	-
	4	0.0	0.0	0.0	0.0	-	-
	5	0.0	0.0	0.0	0.0	-	-
	6	0.0	0.0	0.0	0.0	-	-
423	1	5.9	44.14	37.24	18.62	0.790	2.00
	2	1.4	33.24	45.09	21.67	0.498	2.081
	3	0.4	46.90	53.10	-	0.883	-
	4	0.0	-	-	-	-	-
	5	0.0	0.0	0.0	0.0	-	-
	6	0.0	0.0	0.0	0.0	-	-
473	1	6.2	21.93	55.42	22.65	0.281	2.447
	2	2.8	22.99	54.02	22.99	0.299	2.350
	3	0.4	-	75	25	-	3.0
	4	0.0	0.0	0.0	0.0	-	-
	5	0.0	0.0	0.0	0.0	-	-
	6	0.0	0.0	0.0	0.0	-	-
523	1	14.5	21.42	51.22	27.36	0.273	1.872
	2	3.5	23.34	53.78	22.88	0.304	2.351
	3	1.6	23.59	53.56	22.85	0.305	2.341
	4	2.1	20.42	61.08	18.50	0.257	3.302
	5	1.3	28.91	55.42	15.67	0.407	3.537
	6	1.1	28.52	56.68	14.80	0.400	3.830

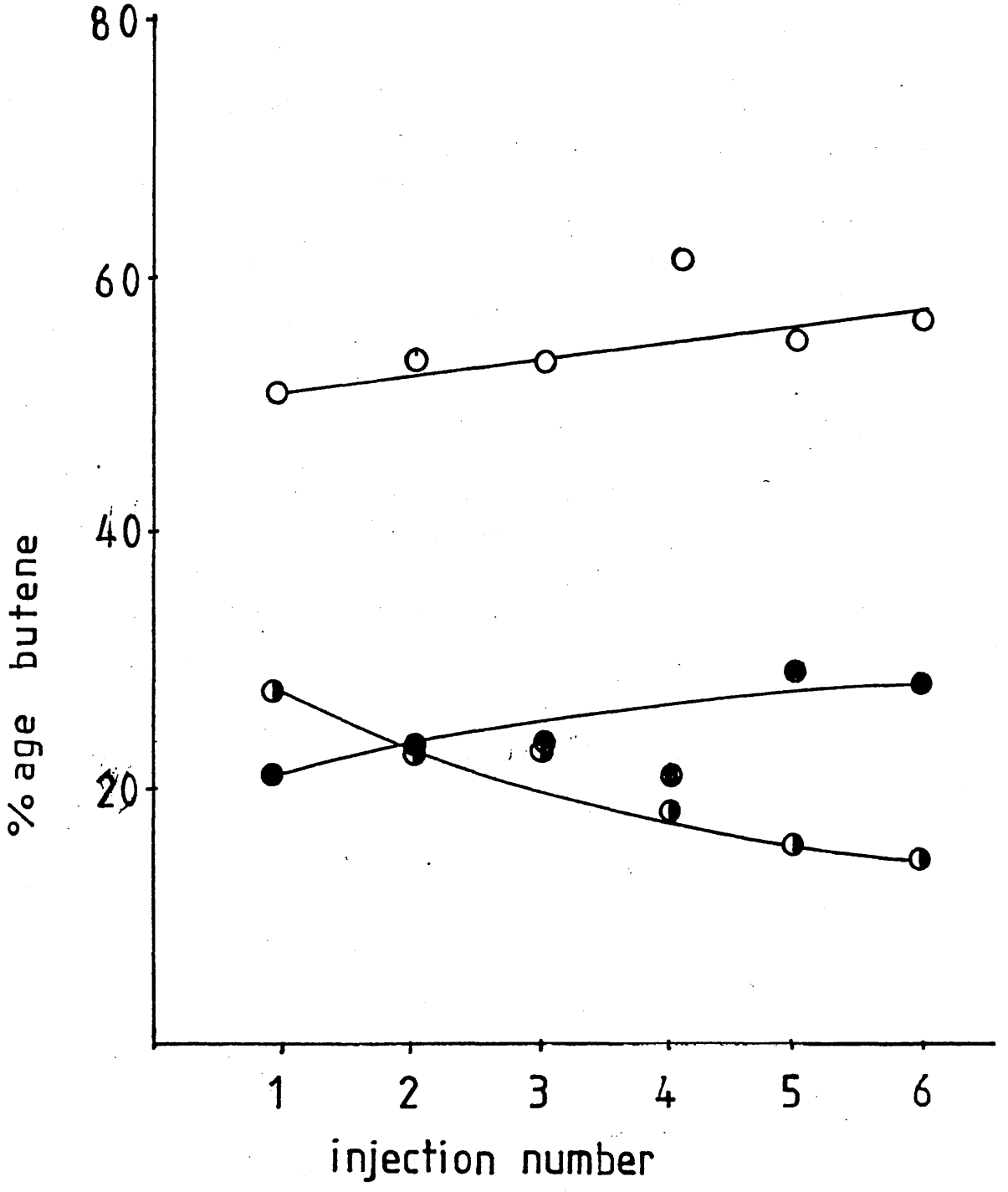


Figure 5.3.

Variation of Butene Distribution with Injection Number at 523K.

(● =1-b, ○= t-2-b, ◑= c-2-b.)

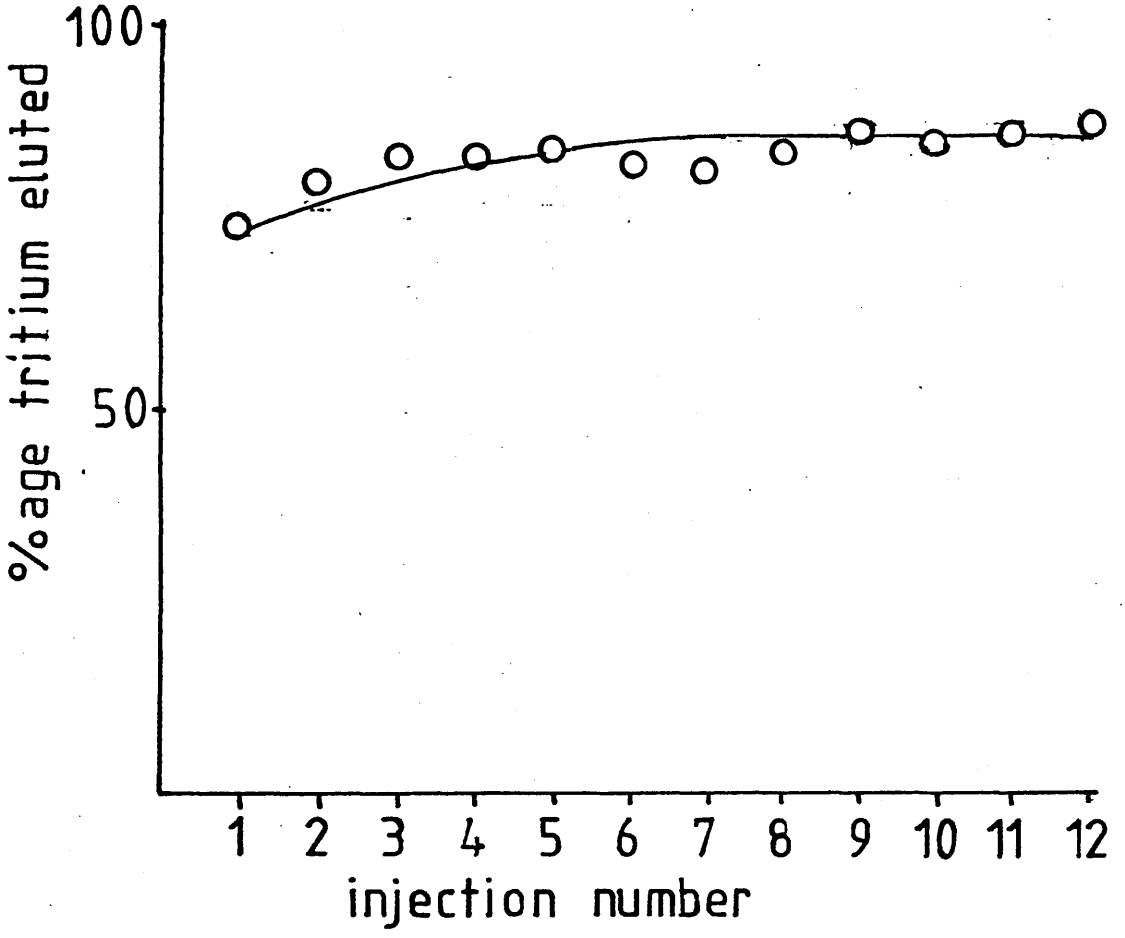


Figure 5.4.

The Tritiation of 0.25g 5% Pd/SiO_2 Catalyst

By 1ml Aliquots

The amount of tritium exchanged was calculated from a comparison of the eluant count and the count observed when a pulse of tritium was passed directly into the counter, without contact with the catalyst. The amount of tritium exchanged in a typical experiment is shown in table 5.6.

5.5. Reaction of Butadiene on Tritiated 5% Pd/SiO_2 Catalysts.

The reaction of butadiene on a tritium-exchanged 5% Pd/SiO_2 catalyst was carried out in a similar manner to that described in section 4.5 for Pt/SiO_2 catalysts.

A catalyst charge of 0.25g was used, and the residual hydrogen on the catalyst was exchanged using successive 1ml injections of tritium. Tritium exchange was carried out until constant eluant activity had been achieved and shown to be reproducible. Normally, six or eight injections of tritium were required.

The product distribution and the radioactive content of each of the various products in each of a series of reactions at temperatures between 323K and 523K are shown in table 5.7. The tritium number (T.No.) is as defined in chapter four.

TABLE 5.6.

The Exchange of Successive 1ml Aliquots of Tritium on a 5% Pd/SiO_2 catalyst

Aliquot Number	μl Tritium exchanged	Cumulative μl Tritium	Exchange atoms T x 10^{-19}
1	249.35	249.3	1.341
2	211.0	460.3	2.475
3	162.9	623.2	3.351
4	166.7	789.9	4.248
5	156.8	946.7	5.091
6	188.3	1135.0	6.104
7	185.0	1320.0	7.099
8	163.1	1483.1	7.976
9	129.0	1612.1	8.669
10	145.8	1757.9	9.453
11	130.0	1887.9	10.153
12	123.7	2011.6	10.818

TABLE 5.11.

Self-hydrogenation of Butadiene on Tritiated 5% Pd/SiO_2.

Temp K	Reaction No.	n-but		1-but		t-2-b		c-2-b		1,3-but	
		µl	T.No.	µl	T.No.	µl	T.No.	µl	T.No.	µl	T.No.
323	1	0.0	0.0	0.4	*	0.1	*	T	-	199.0	0.000
	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	220.0	0.008
	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	224.4	0.020
	4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	230.9	0.010
	5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	231.1	*
373	1	0.0	0.0	3.7	0.0	2.45	*	1.4	0.261	187.8	0.006
	2	0.0	0.0	0.76	*	0.95	1.28	0.31	*	193.2	0.008
	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	196.8	0.008
	4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	202.6	*
	5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**	0.0
	6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	209.7	0.0
423	1	0.9	0.516	7.0	0.726	6.9	0.974	4.1	0.974	156.5	0.084
	2	0.0	0.0	0.6	1.412	1.02	1.402	0.34	1.466	219.1	0.060
	3	0.0	0.0	T	-	0.51	0.0	T	0.0	220.1	0.028
	4	0.0	0.0	T	0.0	T	0.0	T	0.0	231.8	0.034
	5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	220.5	0.036
	6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	218.6	0.058

TABLE 5.7. contd.

Temp K	Reaction No.	n-but μl	n-but T.No.	1-but μl	1-but T.No.	t-2-but μl	t-2-but T.No.	c-2-but μl	c-2-but T.No.	1,3-but μl	1,3-but T.No.
473	1	4.12	0.492	5.43	0.134	9.76	0.164	5.89	0.134	149.9	0.014
	2	0.0	0.0	1.13	*	2.52	0.0	0.79	0.0	219.4	0.016
	3	0.0	0.0	0.47	0.0	1.36	0.0	0.32	0.0	217.7	0.007
	4	0.0	0.0	0.41	0.0	1.20	0.0	0.24	0.0	226.1	0.008
	5	0.0	0.0	T	0.0	0.80	0.0	T	0.0	220.8	0.005
	6	0.0	0.0	0.0	0.0	T	-	0.0	0.0	225.4	0.003
523	1	2.44	0.632	5.77	0.282	12.72	0.220	6.62	0.372	155.5	0.036
	2	0.0	0.0	3.11	0.146	5.36	0.160	2.39	0.342	214.8	0.036
	3	0.0	0.0	1.65	*	2.99	*	1.17	0.0	155.0	0.060
	4	0.0	0.0	2.31	0.0	4.88	0.0	2.28	0.0	148.4	0.030
	5	0.0	0.0	2.47	0.0	4.04	0.0	1.74	0.0	209.9	0.018
	6	0.0	0.0	1.43	0.0	1.35	0.0	0.33	0.0	211.8	0.004

* Accumulated errors in counting and measuring very high or counts less than expected error levels.

** Not measured.

CHAPTER SIX

THE INTERACTION OF BUTADIENE WITH 5% RHODIUM-SILICA CATALYSTS

6.1. Introduction

A series of investigations, similar to those described in chapters four and five for platinum-silica and palladium-silica catalysts respectively, was carried out using regenerated samples of a 5% rhodium-silica catalyst.

6.2. The Retention of Butadiene on 5% Rh/SiO_2 catalysts

The extent to which butadiene was retained on 5% rhodium-silica catalysts was investigated over the temperature range 323K to 523K. Successive 500 μl aliquots of butadiene were injected onto a 0.50g sample of catalyst at each temperature, and the amount of hydrocarbon eluted from the catalyst was measured by gas chromatography.

The volume of butadiene retained and the percentage retention of butadiene following each injection is shown for a series of injections at each temperature in table 6.1. As with 5% Pt/SiO_2 and 5% Pd/SiO_2 catalysts, the volume of hydrocarbon eluted is expressed as 'μl of butadiene equivalent'. However, in the case of rhodium-silica catalysts, a significant part of the eluant at some stages of the reaction is comprised of short-chain hydrocarbons, principally methane, but also ethane, ethylene, propane and propylene. Where this occurred, the measured volumes of these short-chain hydrocarbons were corrected to their C_4 equivalents by multiplying by factors of 0.25, 0.50, 0.75 respectively for C_1-, C_2- and C_3- eluants, before being summed to give the 'butadiene equivalent'. In this way, the carbon balance is seen to be maintained, although the

TABLE 6.1.

Butadiene Retention on Regenerated 5% Rh/SiO_2 (500 µl aliquots).

Temp K.	Injection No.	Hydrocarbon* eluted (µl)	1,3-Butadiene retained (µl)	1,3-Butadiene retained (%)
323	1	0.0	500.0	100.0
	2	0.0	500.0	100.0
	3	103.2	396.8	79.36
	4	289.7	210.3	42.06
	5	381.9	118.1	23.62
373	1	0.0	500.0	100.0
	2	88.5	411.5	82.3
	3	316.2	183.8	36.76
	4	395.9	104.1	20.82
	5	392.4	107.6	21.52
423	1	56.9	443.1	88.62
	2	138.0	362.0	72.40
	3	246.4	253.6	50.72
	4	400.1	99.9	19.98
	5	401.8	98.2	19.64
473	1	51.4	448.6	89.72
	2	69.2	430.8	86.16
	3	71.9	428.1	85.62
	4	336.1	163.9	32.78
	5	429.2	61.8	12.36
523	1	10.5	489.5	97.90
	2	31.9	468.1	93.62
	3	98.2	401.8	80.36
	4	108.0	392.0	78.40
	5	142.6	357.4	71.48

* Expressed as "µl butadiene equivalent".

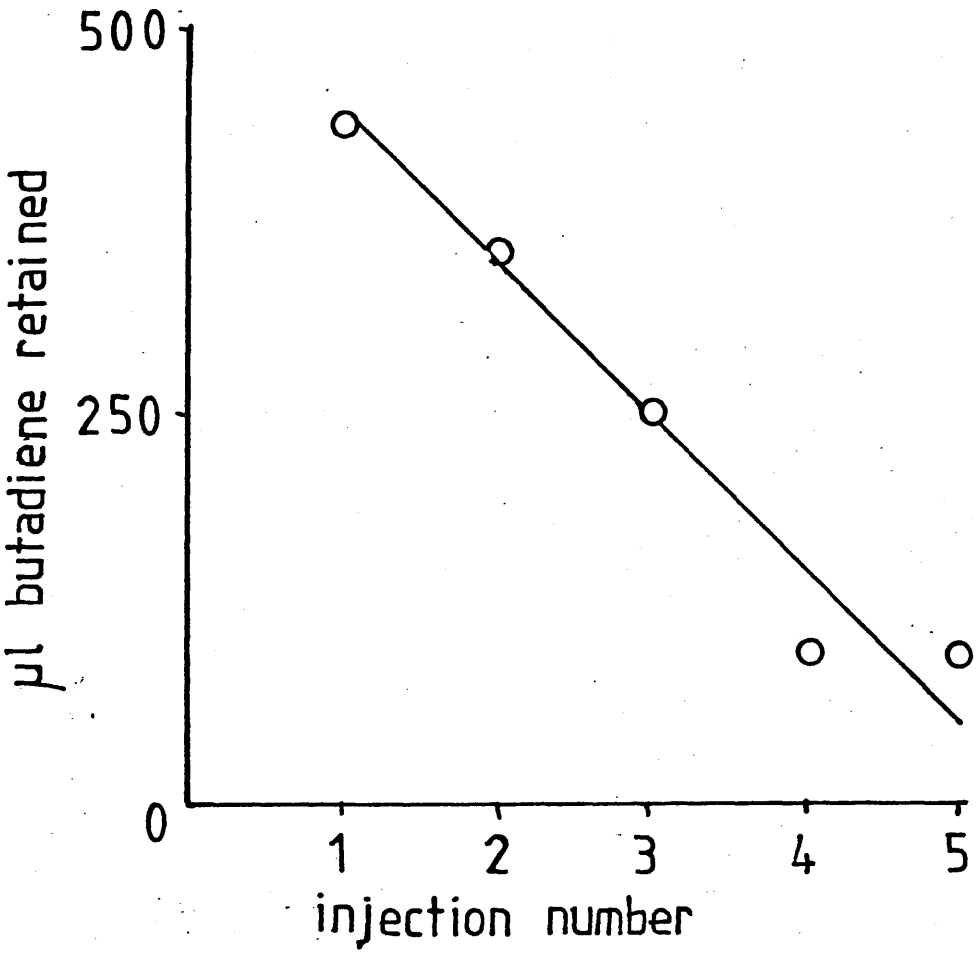


Figure 6.1.

Retention of 500µl Aliquods of Butadiene on 5% Rh/SiO_2 at 423K.

discrepancies introduced into the hydrogen balance are much greater than in the platinum-silica and palladium-silica investigations, especially as unconverted butadiene is not usually a significant constituent of the eluant until the third or fourth injection.

Retention of butadiene is greatest following the first injection at each temperature, and generally decreases with successive injections. This is shown in figure 6.1. for retention at 423K. The amount of butadiene retained following the first injection at each temperature is expressed as a percentage in table 6.2. The retention of butadiene at 323K is especially remarkable as no eluant is detected until the third injection, implying that the catalyst can adsorb at least 1ml (2.7×10^{19} molecules) of butadiene before any hydrogenation takes place.

The cumulative retention for four successive injections at each temperature is shown in table 6.3, and the cumulative retention is shown as a function of temperature in figure 6.2. Cumulative retention decreases with temperature between 323K and 423K and then rises to a maximum at 523K.

6.3. The Self-hydrogenation of Butadiene on 5% Rh/SiO_2 catalysts.

The self-hydrogenation of butadiene on a 5% Rh/SiO_2 catalyst was studied by injecting successive 500 μl samples of butadiene into the helium carrier gas flowing over the catalyst and determining the amounts of the various products in the reactor eluant. A catalyst charge of 0.50g was used, and the self-hydrogenation was studied at various temperatures between 323K and 523K. The catalyst was regenerated after each series of reactions.

TABLE 6.2.

% Retention of 1st 500 µl Aliquot of Butadiene on regenerated 5% Rh/SiO_2 (0.50g).

Temp K	%age Retention
323	100.0
373	100.0
423	88.62
473	89.72
523	97.90

TABLE 6.3.

Cumulative Retention from 4 x 500 µl Aliquots of Butadiene on 0.50g of Regenerated 5% Rh/SiO_2.

Temp K	Cumulative µl	Retention molecules/g catalyst
323	1607.1	8.642×10^{19}
373	1199.4	6.450×10^{19}
423	1158.6	6.231×10^{19}
473	1471.4	7.913×10^{19}
523	1751.4	9.418×10^{19}

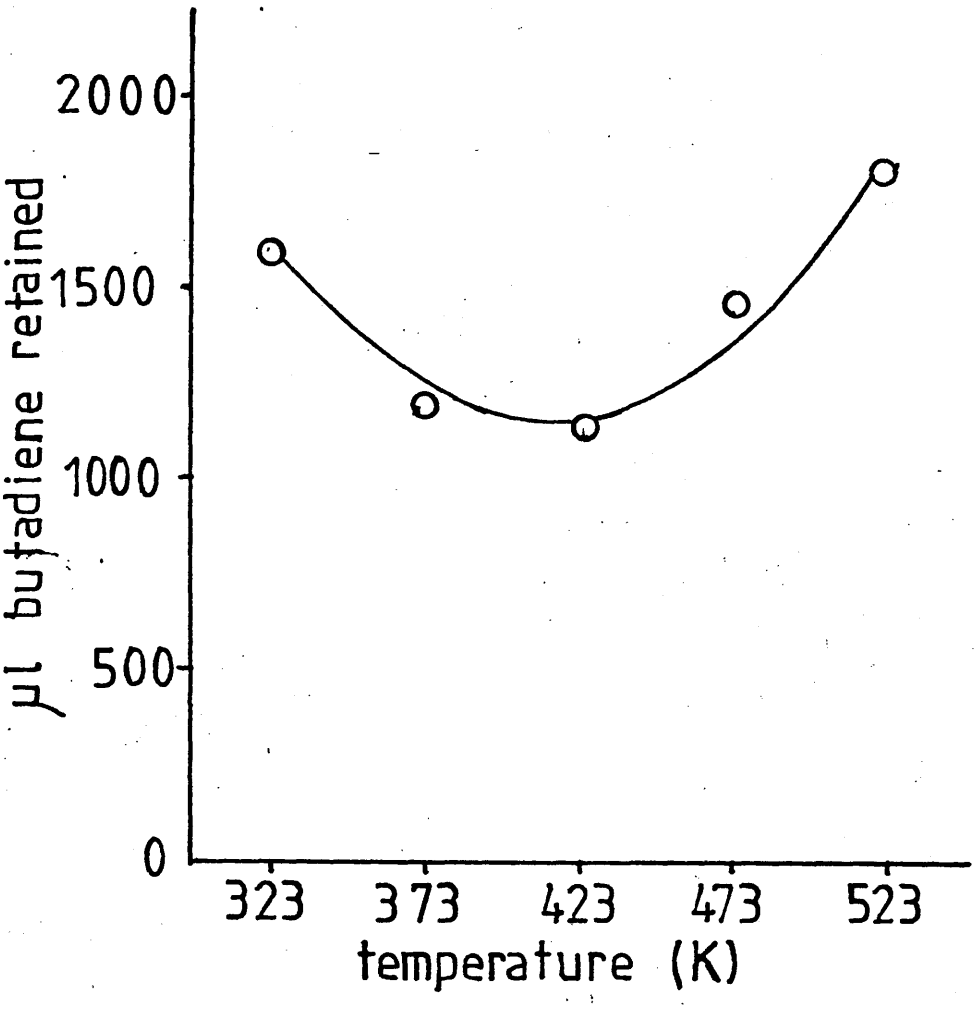


Figure 6.2.

Cumulative Retention of Butadiene

on 5% Rh/SiO_2

The eluant was found to contain methane, ethane, ethylene, propane and propylene, as well as n-butane, the three n-butenes and unreacted butadiene, the relative amounts of each depending upon the number of injections which had been made on to the catalyst. Table 6.4 shows the complete analysis of the eluant from successive reactions at each temperature.

Methane is formed to the greatest extent in the initial reactions at each temperature, and methane formation increases with temperature. The yield of n-butane is also highest in the initial reactions of a particular series but decreases with increasing temperature. The n-butenes do not normally appear in the initial reactions, nor does unreacted butadiene. These are not normally found in the reaction eluant until methane formation has virtually ceased, usually from the third or fourth reaction at each temperature. No hydrocarbon eluant is detected on the first two reactions at 323K or on the first reaction at 373K.

The butene distribution in the reactor eluant is given for a series of injections at each temperature in table 6.5. At 323K and 373K, but-1-ene is the most abundant of the three butenes, but at 423K and above trans-but-2-ene is the most abundant butene. Cis-but-2-ene is formed in lowest yield, of the three butenes, at each temperature studied.

6.4. Tritiation at 5% Rh/SiO_2 catalysts

The residual hydrogen retained on the catalyst following the reduction process was exchanged with tritium using the flow exchange method. Successive 500 μl aliquots of tritium were injected into the helium carrier gas flowing over the catalyst at 633K. 500 μl

TABLE 6.4.

The Self-hydrogenation of Butadiene on 5% Rh/SiO_2.

T (K)	Inj. No.	CH_4	C_2H_6/H_4	C_3H_8	C_3H_6	n-but	1-but	t-2-b	c-2-b	1,3-but	µl but retained
323	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	500.0
	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	500.0
	3	0.1	3.2	0.3	0.0	101.4	0.0	0.0	0.0	0.0	396.8
	4	0.0	0.0	0.0	0.0	4.4	26.4	13.2	11.9	233.9	210.3
	5	0.0	0.0	0.0	0.0	0.0	6.3	3.1	0.3	302.2	188.1
	6	0.0	0.0	0.0	0.0	0.0	T	T	T	388.0	112.0
373	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	500.0
	2	40.3	32.5	19.8	0.1	47.2	0.0	0.0	0.0	0.0	411.5
	3	1.7	1.9	0.2	T	19.5	31.6	29.5	19.3	214.8	183.8
	4	0.0	0.0	T	0.0	T	15.7	14.2	9.8	356.2	104.1
	5	0.0	0.0	0.0	0.0	0.0	10.2	6.9	6.4	368.9	107.6
423	1	227.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	443.1
	2	551.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	362.0
	3	50.4	21.0	6.1	0.5	23.6	27.9	33.6	18.9	114.4	253.6
	4	0.0	T		0.6	0.3	14.5	20.3	9.9	354.7	99.9
	5	0.0	T	T	T	T	12.5	16.3	7.9	365.1	98.2
	6	0.0	0.0	0.0	0.0	0.0	7.4	9.9	5.2	416.6	61.0
	7	0.0	0.0	0.0	0.0	0.0	4.4	3.8	1.8	418.5	71.5

TABLE 6.4. contd.

T (K)	Inj. No.	CH_4	C_2H_6/C_2H_4	C_3H_8	C_3H_6	n-but	1-but	t-2-but	c-2-but	1,3-but	1 but retained
473	1	306.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	423.8
	2	385.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	403.7
	3	379.0	2.3	1.5	0.9	16.9	T	5.4	3.4	0.0	376.6
	4	T	T	0.3	1.7	4.2	17.7	25.0	14.2	163.5	273.9
	5	0.0	T	T	1.1	0.1	12.1	19.0	8.5	294.2	165.3
	6	0.0	0.0	0.0	0.0	0.0	10.3	11.3	4.3	305.7	168.4
	7	0.0	0.0	0.0	0.0	0.0	11.2	10.3	4.2	321.0	153.3
523	1	41.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	489.5
	2	127.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	468.1
	3	392.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	401.8
	4	432.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	392.0
	5	192.7	1.7	0.5	3.7	5.8	19.7	40.9	24.0	0.0	357.4
	6	T	T	T	5.9	1.0	36.2	44.3	25.2	187.1	201.8

TABLE 6.5.

Analysis of Butene Distribution for reaction of Butadiene on 5% Rh/SiO_2.

Temp K	Reaction No.	% butenes 1-b	t-2-b	c-2-b	1-b / 2-b	t-2-b / c-2-b
323	1	-	-	-	-	-
	2	-	-	-	-	-
	3	-	-	-	-	-
	4	51.26	25.63	23.11	1.05	1.11
	5	64.95	31.96	3.09	1.85	10.33
373	1	-	-	-	-	-
	2	-	-	-	-	-
	3	39.30	36.69	24.01	0.648	1.53
	4	39.55	35.77	24.68	0.654	1.49
	5	43.40	29.36	27.23	0.767	1.08
423	1	-	-	-	-	-
	2	-	-	-	-	-
	3	34.70	41.79	23.51	0.531	1.78
	4	32.44	45.41	22.15	0.480	2.05
	5	34.06	44.41	21.52	0.516	2.06
	6	32.89	44.00	23.11	0.490	1.90
	7	44.00	38.00	18.00	0.786	2.11
473	1	-	-	-	-	-
	2	-	-	-	-	-
	3	0.0	61.36	38.63	0.0	1.59
	4	31.11	43.94	24.96	0.452	1.76
	5	30.56	47.98	21.46	0.494	2.24
	6	39.77	43.63	16.60	0.660	2.63
	7	43.58	40.07	16.34	0.772	2.45
523	1	-	-	-	-	-
	2	-	-	-	-	-
	3	-	-	-	-	-
	4	-	-	-	-	-
	5	23.29	48.34	28.37	0.304	1.70
	6	34.25	41.91	23.84	0.521	1.76

aliquots were used as it was observed that most of the exchange occurred following the first two or three millilitres of tritium. It was also noticed that the count rate took between ten and fifteen minutes to return to the background level after passing an aliquot of tritium over the catalyst. This was very much longer than the five minutes required during the investigations with the 5% Pt/SiO_2 and 5% Pd/SiO_2 catalysts.

As was the case with the two catalysts previously studied, the eluant activity reached a constant level after the first few injections. The variation in the amount of tritium eluted from the catalyst with successive injections of tritium is shown in figure 6.3. The amount of tritium exchanged in a typical experiment is shown in table 6.6.

6.5. Self-hydrogenation of Butadiene on Tritiated 5% Rh/SiO_2.

The role played by residual hydrogen retained on the catalyst following the regeneration of the catalyst, or associated with the support as surface hydroxyl groups, in the reactions discussed in section 6.3 was investigated by carrying out reactions on tritium-exchanged catalysts.

The tritium exchange was carried out as described in section 6.4., exchange being carried out until constant eluant activity had been attained and demonstrated to be reproducible. Normally between six and eight millilitres of tritium were required.

The catalyst (0.50g) was then cooled to the reaction temperature and reactions carried out by injecting successive 500 μl aliquots of butadiene into the helium carrier gas flowing over the catalyst. The

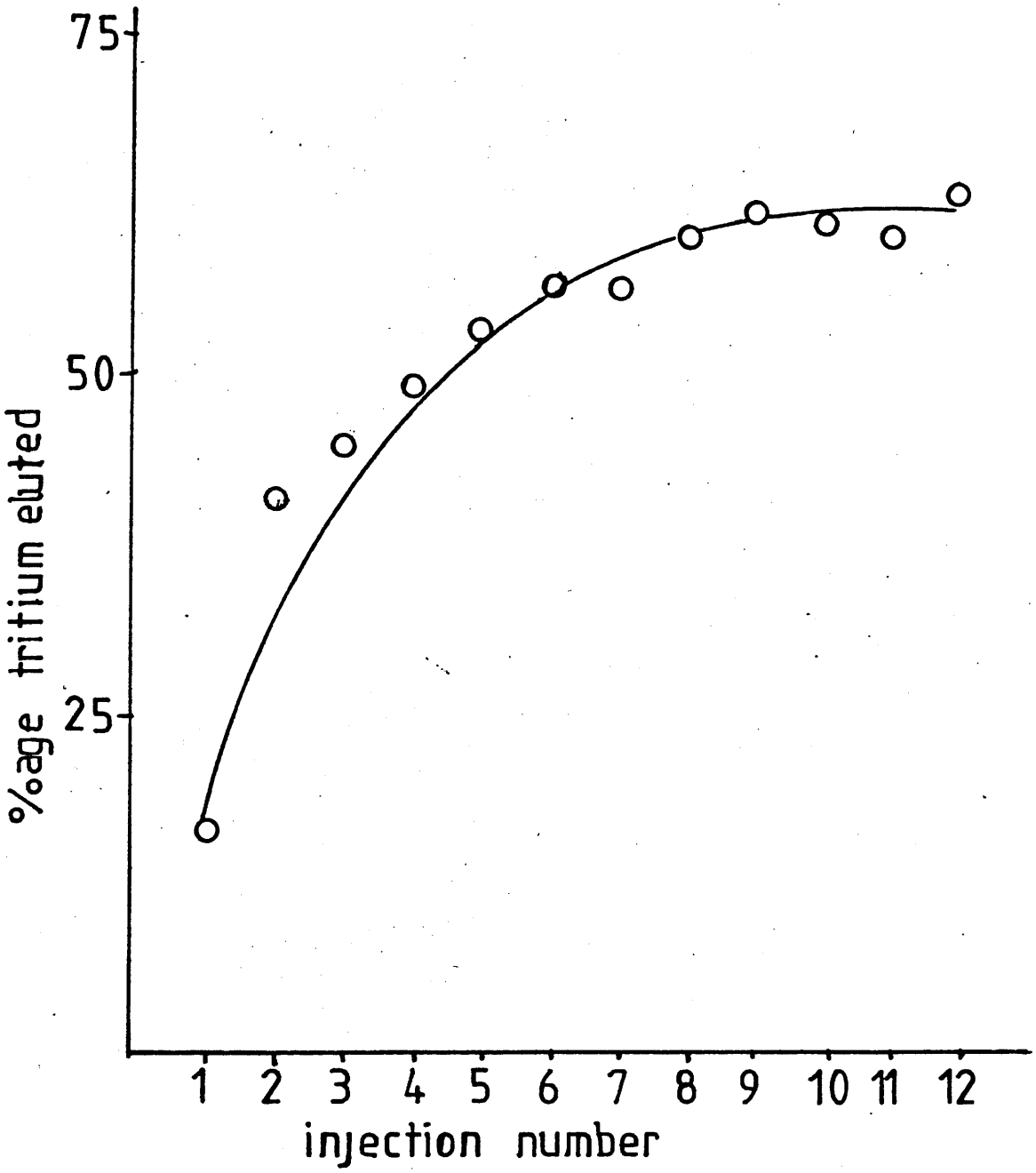


Figure 6.3.

Tritiation of 0.5g 5% Rh/SiO_2 by 500μl Aliquots.

TABLE 6.6.

The Exchange of Successive 500 μl Aliquots of Tritium on 5% Rh/SiO_2 catalysts.

Aliquot Number	Tritium Exchanged (μl)	Cumulative Tritium Exchanged μl	Cumulative Tritium Exchanged atoms x 10^{-19}
1	421.0	421.0	2.264
2	345.6	766.6	4.123
3	274.8	1041.4	5.600
4	253.1	1294.5	6.961
5	232.2	1526.7	8.2101
6	215.2	1741.9	9.367
7	216.0	1957.9	10.529
8	195.7	2153.6	11.581
9	193.5	2347.1	12.622
10	193.1	2540.2	13.660
11	191.3	2731.5	14.689
12	182.8	2914.3	15.672

eluant was then analysed by gas chromatography and the radioactivity of the separated products measured by proportional counting.

Table 6.7 shows the product distribution and the radioactive contents of the individual products (expressed as tritium number) of a series of successive reactions at various temperatures between 323K and 473K.

TABLE 6.7.

Self-hydrogenation of Butadiene on Tritiated 5% Rh/SiO_2

a) Reactions at 323K

Reaction Number	Product	Volume μl	Tritium Number
1	NO ELUANT	-	-
2	NO ELUANT	-	-
3	CH_4	T	-
	C_2H_6/C_2H_4	3.1	-
	C_3H_8	T	-
	n-b	101.4	0.508
4	n-b	4.4	-
	1-b	26.4	0.250
	t-2-b	13.2	0.178
	c-2-b	11.9	0.00
	1,3-b	233.9	0.00
5	1-b	6.3	0.352
	t-2-b	3.1	*
	c-2-b	0.3	*
	1,3-b	302.2	0.012
6	1-b	T	-
	t-2-b	T	-
	c-2-b	T	-
	1,3-b	388.0	0.00

TABLE 6.7 contd.

b) Reactions at 373K.

Reaction Number	Product	Volume μl.	Tritium Number
1	NO ELUANT		
2	CH_4	40.3	) **
	C_2H_6/C_2H_4	32.5	) **
	C_3H_8	19.8	) **
	C_3H_6	0.1	0.00
	n-b	47.2	0.350
3	CH_4	1.7	0.00
	C_2H_6/C_2H_4	1.9	0.00
	C_3H_8	0.2	0.00
	C_3H_6	T	-
	n-b	19.5	0.082
	1-b	31.6	0.086
	t-2-b	29.5	0.136
	c-2-b	19.3	0.002
	1,3-b	214.8	0.020
4	C_3H_8	T	-
	n-b	T	-
	1-b	15.7	0.196
	t-2-b	14.2	0.000
	c-2-b	9.8	0.170
	1,3-b	356.2	0.004
5	1-b	10.2	0.068
	t-2-b	6.9	0.173
	c-2-b	6.4	0.278
	1,3-b	368.9	0.000

TABLE 6.7. contd.

c) Reactions at 423K.

Reaction Number	Product	Volume μl	Tritium Number
1	CH_4	227.6	0.72
2	CH_4	551.9	0.080
3	CH_4	50.4	0.00
	C_2H_6/C_2H_4	21.0	0.00
	C_3H_8	6.1	0.00
	C_3H_6	0.5	-
	n-b	23.6	0.00
	1-b	27.9	0.087
	t-2-b	33.6	0.068
	c-2-b	18.9	0.037
	1,3-b	111.4	0.002
4	1-b	14.5	0.000
	t-2-b	20.3	0.205
	c-2-b	9.9	0.00
	1,3-b	354.7	0.002
5	1-b	12.5	0.00
	t-2-b	16.3	0.00
	c-2-b	7.9	0.00
	1,3-b	365.1	0.005
6	1-b	7.4	0.00
	t-2-b	9.9	0.00
	c-2-b	5.2	0.00
	1,3-b	416.6	0.004

TABLE 6.7. contd.

d) Reactions at 473K.

Reaction Number	Product	Volume μl	Tritium Number
1	CH_4	238.1	1.388
2	CH_4	298.8	0.254
3	CH_4	379.0	0.100
	C_2H_6/C_2H_4	2.3	*
	C_3H_8	1.5	*
	n-b	16.9	0.362
	1-b	T	-
	t-2-b	5.4	0.369
	c-2-b	3.4	0.479
4	n-b	4.2	1.470
	1-b	17.7	0.360
	t-2-b	24.9	0.488
	c-2-b	14.2	0.382
	1,3-b	163.5	0.072
5	n-b	T	-
	1-b	12.1	0.485
	t-2-b	19.0	0.600
	c-2-b	8.5	1.078
	1,3-b	294.2	0.062
6	1-b	10.2	0.420
	t-2-b	11.3	0.562
	c-2-b	4.3	1.394
	1,3-b	305.7	0.042
7	1-b	9.3	0.436
	t-2-b	10.3	0.640
	c-2-b	4.2	1.278
	1,3-b	321.0	0.034

* counts less than expected background.

** these three eluants non-resolvable on ratemeter trace. Average Tritium Number = 0.4.

CHAPTER SEVEN

THE INTERACTION OF BUTADIENE WITH FRESH 5% PLATINUM-SILICA CATALYSTS.

7.1 Introduction

The investigations described in this chapter were carried out on freshly reduced samples of catalyst. After each series of reactions at each temperature, the catalyst sample was replaced.

7.2. The Retention of Butadiene on fresh 5% Pt/SiO_2 Catalysts.

The retention of butadiene on a series of freshly reduced 5% platinum-silica catalysts was investigated over the temperature range 373K to 573K. Successive 500 μl aliquots of butadiene were injected into the helium carrier gas stream flowing over the catalyst, and the amount of butadiene retained following each injection was calculated by measuring the volume of hydrocarbon eluted by gas chromatography. The catalyst charge used was 0.50g at each temperature.

Table 7.1 shows the volume of hydrocarbon eluted and the volume of butadiene retained following each of a series of five injections of butadiene at the various temperatures. The volume of butadiene retained is also expressed as a percentage of the injected amount. At each temperature, the retention is greatest following the initial injection and then decreases to an approximately steady value, which is different for each temperature. This is shown for the adsorption at 523K in figure 7.1.

Table 7.2. lists the percentage retention of the initial pulse of butadiene at each temperature, and shows this to rise to a maximum at 473K and then to decrease in an irregular manner.

TABLE 7.1.

Butadiene Retention on fresh 5% Pt/SiO_2 (500 µl aliquots)

Temp K	Injection No.	Hydrocarbon eluted (µl)	1,3-butadiene retained (µl)	1-3 butadiene retained (%)
373	1	353.2	146.8	29.82
	2	477.2	22.8	2.48
	3	479.6	20.4	1.12
	4	498.6	1.4	0.73
	5	498.1	1.9	0.62
423	1	288.6	211.4	42.28
	2	407.9	92.1	18.43
	3	466.3	33.7	6.74
	4	449.3	50.7	10.13
	5	436.7	63.3	12.65
473	1	226.6	273.4	54.68
	2	478.0	22.0	4.41
	3	500.0	0.0	0.0
	4	476.5	23.5	4.70
	5	479.0	21.0	4.20
523	1	306.6	193.4	38.67
	2	438.1	61.9	12.38
	3	482.8	17.2	3.44
	4	480.4	19.6	3.92
	5	481.8	18.2	3.64
573	1	286.4	213.6	42.73
	2	442.9	57.1	11.42
	3	460.0	40.0	8.00
	4	470.0	30.0	6.18
	5	474.2	25.8	5.15

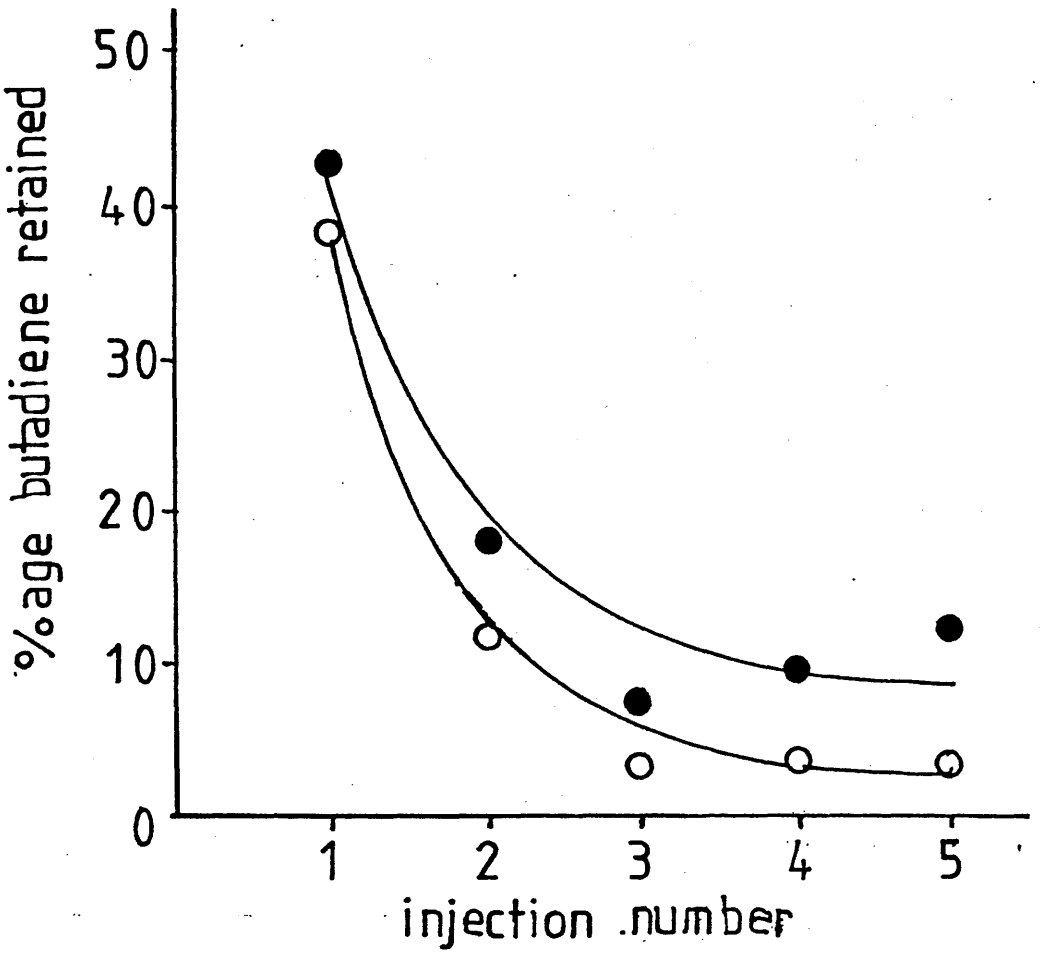


Figure 7.1.

The Retention of Butadiene on

Fresh 5% Pt/SiO_2 Catalysts.

(● =423K, O = 523K.)

TABLE 7.2.

%age Retention on 1st 500 μl Aliquot of Butadiene on fresh 5% Pt/SiO_2.

Temp K	%age Retention
373	29.82
423	42.28
473	54.68
523	38.67
573	42.73

TABLE 7.3.

Cumulative Retention from 4 x 500 μl aliquots of Butadiene on 0.50g 5% Pt/SiO_2 (Fresh).

Temp K	Cumulative μl	Retention molecules/g catalyst
373	191.3	1.029×10^{19}
423	387.9	2.086×10^{19}
473	339.9	1.715×10^{19}
523	292.1	1.571×10^{19}
573	340.7	1.832×10^{19}

Table 7.3 shows the cumulative retention of butadiene from the first four injections at each temperature expressed as microlitres of butadiene retained and as molecules of butadiene retained per gram of catalyst. This is seen to be a maximum at 373K and a minimum at 423K.

7.3. The Self-hydrogenation of Butadiene on freshly reduced 5% Pt/SiO_2 catalysts.

The self-hydrogenation of butadiene was studied by injecting successive 500 μl samples of butadiene into the helium carrier gas passing over the catalyst and determing the amounts of the various products in the reactor eluant. The self-hydrogenation was studied using freshly reduced samples (0.50g) of the 5% platinum-silica catalyst at various temperatures between 373K and 573K.

The eluant was found to contain n-butane and the three n-butenes as well as unreacted butadiene. Some small amounts of short-chain hydrocarbons also appear in the product following the initial reactions at 523K and 573K. No cracking of the butadiene was observed below 523K. A complete analysis of the eluant from the catalyst is shown in table 7.4.

It is noticeable that, in the reactions carried out at 473K, the total eluant exceeds 500 μl on the third and sixth reactions. This is most probably due to the series of experiments, reported here and in 7.2 above, having been performed using a syringe not fitted with a Chaney adaptor, and so subsequently the reproducibility of the injection is impaired. 'Rounding' errors may also contribute to this seemingly high value.

TABLE 7.4.

The Self-hydrogenation of Butadiene on 0.50g freshly reduced 5% Pt/SiO_2.

Temp K	Injection No.	CH_4	C_2H_6/C_2H_4	C_3H_8	C_3H_6	n-b	1-b	t-2-b	c-2-b	1,3-b
373	1	0.0	0.0	0.0	0.0	45.7	36.3	12.0	10.4	248.8
	2	0.0	0.0	0.0	0.0	0.0	8.45	2.33	1.62	464.8
	3	0.0	0.0	0.0	0.0	0.0	4.31	1.21	0.72	473.4
	4	0.0	0.0	0.0	0.0	0.0	2.26	0.94	0.47	495.0
	5	0.0	0.0	0.0	0.0	0.0	2.11	0.71	0.29	495.0
423	1	0.0	0.0	0.0	0.0	30.4	38.9	16.3	12.6	190.4
	2	0.0	0.0	0.0	0.0	0.0	12.7	5.7	3.96	385.5
	3	0.0	0.0	0.0	0.0	0.0	5.4	2.6	1.9	456.4
	4	0.0	0.0	0.0	0.0	0.0	2.48	1.36	0.9	444.6
	5	0.0	0.0	0.0	0.0	0.0	2.1	1.07	0.8	432.8
473	1	0.0	0.0	0.0	0.0	115.4	28.6	40.8	26.4	15.4
	2	0.0	0.0	0.0	0.0	1.76	34.0	20.0	13.6	408.6
	3	0.0	0.0	0.0	0.0	0.0	16.5	10.0	6.3	485.9
	4	0.0	0.0	0.0	0.0	0.0	15.8	8.1	5.1	447.5
	5	0.0	0.0	0.0	0.0	0.0	7.0	3.9	2.5	465.6
	6	0.0	0.0	0.0	0.0	0.0	4.4	2.8	1.2	495.0
	7	0.0	0.0	0.0	0.0	0.0	4.4	1.8	1.1	481.4

TABLE 7.4. contd.

Temp K	Injection No.	Volume of Gas in Eluted Products (μl)								
		CH_4	C_2H_6/C_2H_4	C_3H_8	C_3H_6	n-b	1-b	t-2-b	c-2-b	1,3-b
523	1	0.0	2.5	0.6	0.6	81.6	49.6	45.7	33.6	93.1
	2	0.0	T	T	T	0.9	24.3	15.7	10.9	368.3
	3	0.0	0.0	0.0	0.0	0.0	12.1	7.3	4.6	458.8
	4	0.0	0.0	0.0	0.0	0.0	9.4	6.0	3.8	461.2
	5	0.0	0.0	0.0	0.0	0.0	7.3	4.4	2.6	467.5
	6	0.0	0.0	0.0	0.0	0.0	5.9	3.7	2.2	449.1
	7	0.0	0.0	0.0	0.0	0.0	3.8	2.4	0.9	453.2
573	1	90.7	23.1	7.3	5.8	44.0	47.6	47.5	32.8	70.4
	2	T	T	T	1.9	4.4	41.1	32.5	20.2	343.3
	3	0.0	0.0	0.0	2.0	2.0	35.7	28.4	16.5	375.9
	4	0.0	0.0	0.0	1.2	0.3	19.5	14.4	8.4	425.6
	5	0.0	0.0	0.0	1.0	0.3	16.8	11.9	7.4	437.1

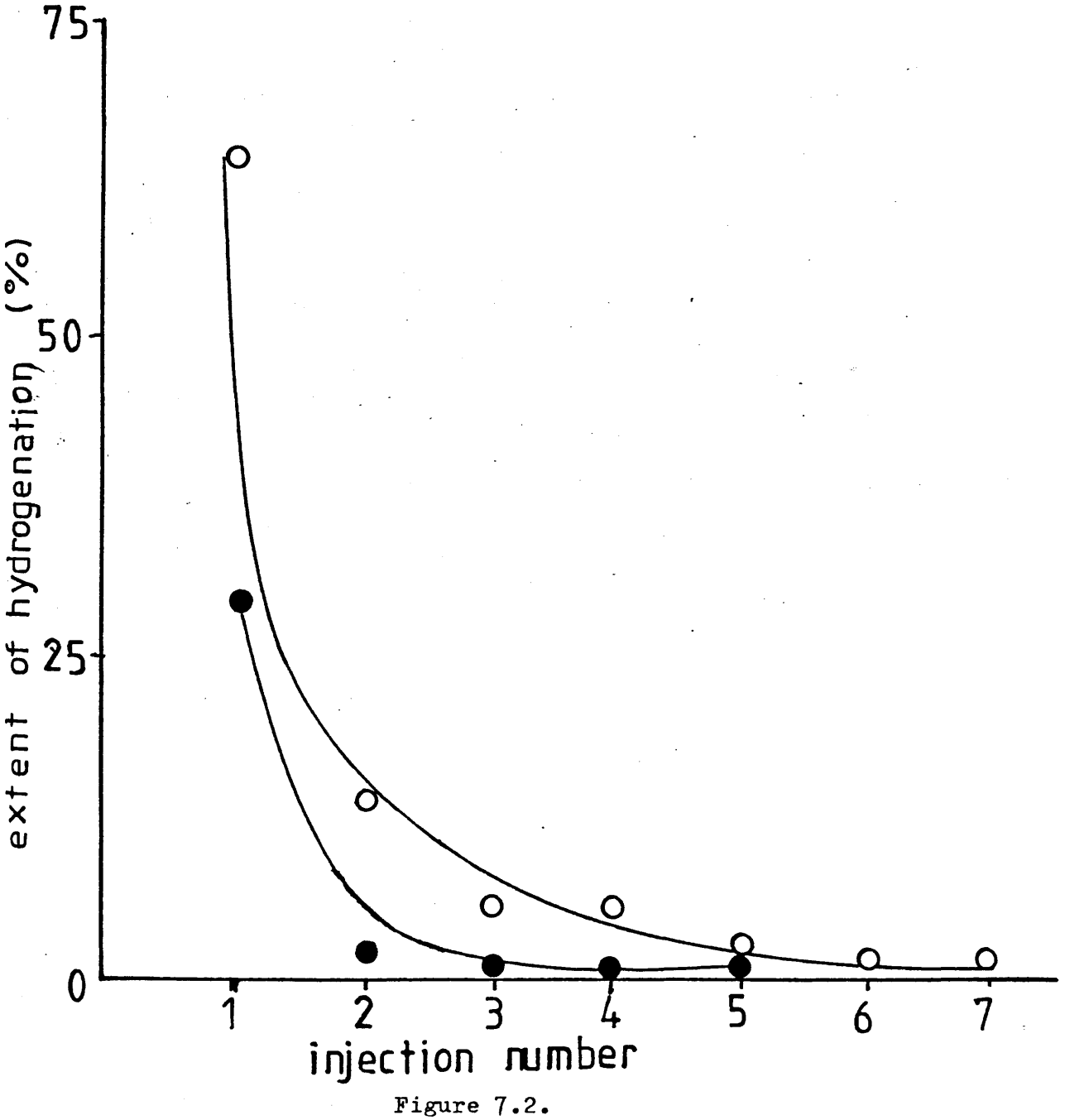


Figure 7.2.

Variation in Extent of Reaction on Successive Reactions.

(● = 373K, ○ = 473K.)

Self-hydrogenation occurs to the greatest extent with the first injection at each temperature, and it is in this first reaction that all, or almost all, of the n-butane formation is observed. The selectivity for n-butene is unity in subsequent reactions, except at high temperature. It is also observed that most of the cracking products, when formed, appear in the eluant from the first reaction. Figure 7.2 shows the decrease in extent of hydrogenation on successive reactions for 373K and 473K which are typical of the behaviour observed at all temperatures.

Table 7.5 shows how the extent of hydrogenation, and the distribution of the three n-butenes vary in successive reactions at each temperature. The extent of hydrogenation is as defined in 4.3 above.

Production of n-butane is greatest at 473K, and but-1-ene is normally observed to be the most abundant butene. Figure 7.3 shows the distribution of the n-butenes and how this varies in successive reactions at each temperature.

TABLE 7.5.

The Variation of Butene Distribution, and Extent of Self-hydrogenation with successive reactions at a variety of Temperatures

Temp K	Reaction No.	Ext.Hyd. %	% 1-b	% t-2-b	% c-2-b	$\frac{1\text{-b}}{2\text{-b}}$	$\frac{t}{c}$
373	1	30.02	61.84	20.44	17.72	1.62	1.15
	2	2.48	68.15	18.79	13.06	2.14	1.44
	3	1.12	69.07	19.39	11.54	2.23	1.68
	4	0.73	61.37	25.75	12.88	1.59	2.00
	5	0.62	67.85	22.83	9.32	2.11	2.45
423	1	25.72	57.37	24.04	18.58	1.35	1.29
	2	4.47	56.80	25.49	17.71	1.31	1.44
	3	1.98	54.54	26.26	19.19	1.20	1.37
	4	0.95	52.37	28.69	18.98	1.10	1.53
	5	0.79	52.90	26.95	20.15	1.12	1.34
473	1	65.32	29.85	42.59	27.56	0.42	1.54
	2	14.22	50.29	29.59	20.12	1.01	1.47
	3	6.56	50.30	30.49	19.21	1.01	1.59
	4	5.80	54.48	27.93	17.58	1.19	1.59
	5	2.68	52.24	29.10	18.66	1.09	1.56
	6	1.68	52.38	33.33	14.29	1.10	2.33
	7	1.46	60.44	24.33	15.25	1.53	1.60
523	1	58.42*	38.48	35.45	26.07	0.62	1.36
	2	10.36	47.74	30.84	21.41	0.91	1.44
	3	4.80	50.42	30.42	19.12	1.02	1.59
	4	3.84	48.96	31.25	19.79	0.96	1.58
	5	2.86	51.05	30.77	18.18	1.04	1.69
	6	2.36	50.00	31.36	18.64	1.00	1.68
	7	1.42	53.52	33.80	12.68	1.15	2.66
573	1	51.98	37.22	37.14	25.64	0.59	1.45
	2	20.52	43.82	34.65	21.53	0.78	1.61
	3	16.92	44.29	35.24	20.47	0.80	1.72
	4	8.58	46.10	34.04	19.86	0.84	1.71
	5	7.34	46.54	33.96	20.50	0.87	1.66

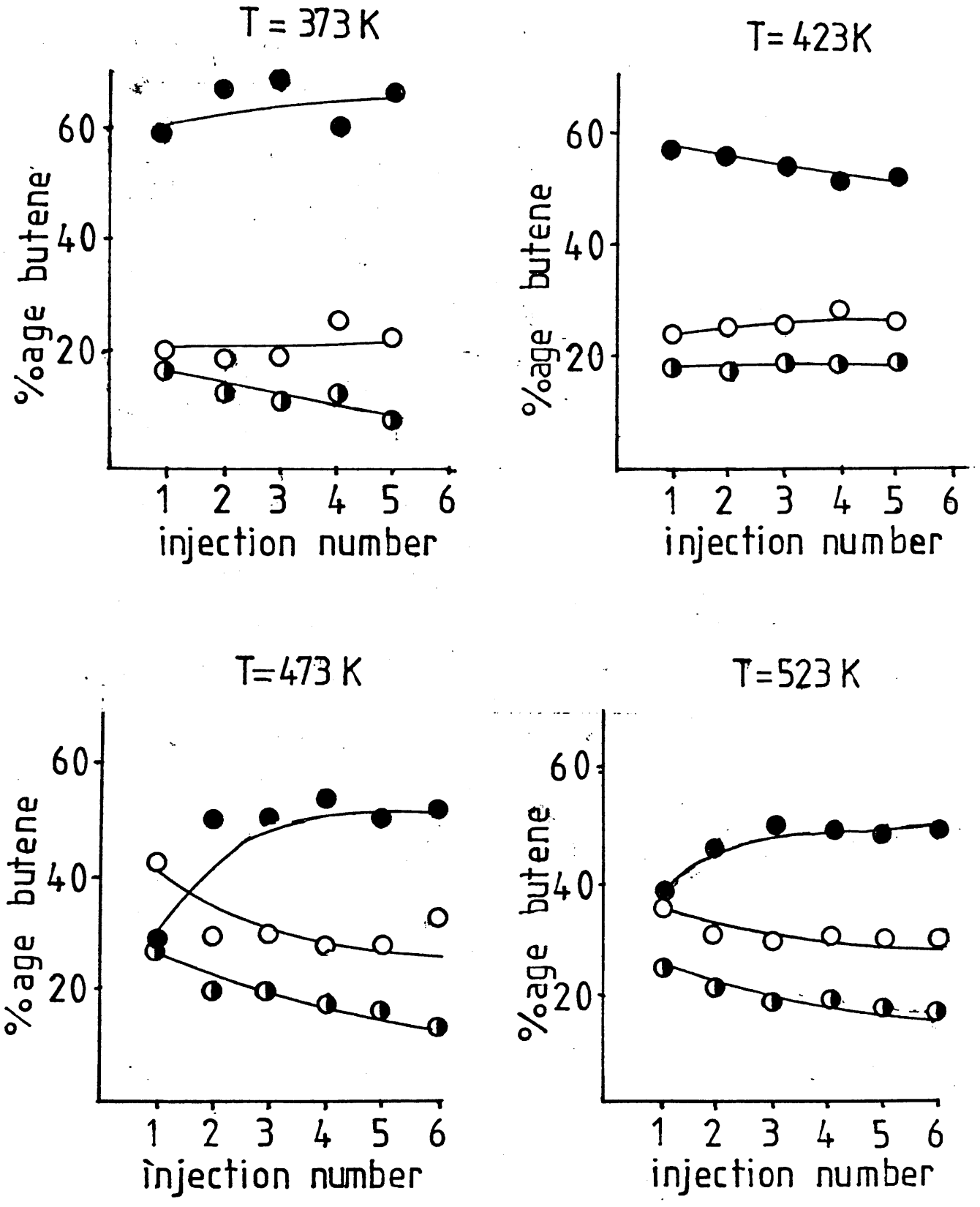


Figure 7.3.

Variation of Butene Distribution

With Injection Number.

(● = 1-b, ○ = t-2-b, ◑ = c-2-b.)

CHAPTER EIGHT

DISCUSSION OF RESULTS

8.1. The Retention and Self-Hydrogenation of Butadiene

Each catalyst used in the present study was found to be active for the retention and self-hydrogenation of butadiene. n-Butane was formed along with the n-butenes on each of the catalysts studied, and carbon-carbon bond fission was observed on Rh/SiO_2, and on Pt/SiO_2 at 523K and above, but not with Pd/SiO_2.

The pattern of butadiene retention was similar on each of the catalysts, with retention being greatest on the initial injection and rapidly decreasing on subsequent injections, to fluctuate about an approximately constant level, the value of which was a function of the catalyst type and temperature. Hydrogenation activity similarly declined with increasing injection number, although this pattern was distorted somewhat on Rh/SiO_2, where cracking reactions were dominant in the early injections.

The initial high value for butadiene retention is regarded as being due to the initially high number of sites for chemisorption. As the surface coverage increases however, the number of sites for 'new' molecules to chemisorb on the surface decreases and so the retention diminishes on the second and subsequent injections. The amount of butadiene injected onto the catalyst at each injection was comparable to the total number of metal atoms present in the catalyst sample, the metal atom to butadiene molecule ratios being 5.7, 10.6, 10.9 for the Pt, Pd and Rh catalysts respectively.

Whilst the total number of surface metal atoms exposed on each catalyst was not determined in the present work, Orozco (64), using

catalysts of the same metal loading, prepared in an identical manner, Measured values for 5% Pt/SiO_2 and 5%Pd/SiO_2 of 2.44×10^{19} and 2.28×10^{19} exposed surface metal atoms per gram of catalyst. The mode of adsorption of CO on Rh is uncertain, but Reid (65) has estimated values of the surface atoms:bulk atoms ratio of 0.37 and 0.19 for the 100% bridged and 100% linear modes of adsorption respectively. On the basis of these figures, it is possible to estimate upper and lower limits for the number of total surface metal atoms on 5% Rh/SiO_2 as 7.89×10^{19} atoms/g.catalyst and 4.66×10^{19} atoms/g.catalyst respectively.

Unreacted butadiene was observed to be eluted along with the hydrogenated products following the first injection on the Pt/SiO_2 and Pd/SiO_2 catalysts. This is interpreted as indicating that most, if not all, of the available sites for butadiene adsorption, have been occupied following the first injection. The pattern of behavior is slightly different in studies of the Rh/SiO_2 catalyst. as unreacted butadiene, and hydrogenated products, are not normally eluted until after the third of fourth injection, it can be concluded that more sites are available for the chemisorption of butadiene on the catalyst surface. This is in accordance with the estimated number of surface metal atoms.

This initially adsorbed butadiene will gradually dissociate togive adsorbed hydrogen and a dissociatively adsorbed hydrocarbon species. The dissociative adsorption of unsaturated hydrocarbons is well documented (19, 21, 23, 66, 67), and dissociation of the adsorbed butadiene is also indicated by the high extent of self-hydrogenation observed following the initial injection on the Pt/SiO_2 and Pd/SiO_2 catalysts.

Previous workers (25, 27, 50) have shown that hydrocarbon which is retained by the catalyst is adsorbed differently from that which is active in hydrogenation, and it has been generally assumed (68) that unsaturated hydrocarbons which are active for hydrogenation are associatively adsorbed. These two modes of adsorption have been correlated with the regions of primary and secondary adsorption observed in the adsorption isotherms of ^{14}C-ethylene and ^{14}C-acetylene on supported metal catalysts (29, 30).

The observation that there is no eluant following the first injection at low temperatures on the Rh/SiO_2 catalyst indicates that a certain extent of surface coverage is required before the self-hydrogenation process can begin. The initially adsorbed butadiene then dissociates gradually to give a dissociatively adsorbed, and therefore strongly retained, monolayer, releasing hydrogen which is active in the hydrogenation of associatively adsorbed molecules of butadiene. At higher temperatures on Rh/SiO_2, the dissociation of butadiene occurs more rapidly, and cracking processes become progressively more important as the temperature increases. Hydrogenation does not begin until the third or fourth injection, even at high temperature, but hydrogenation is observed before the appearance of butadiene in the eluant. This suggests that self-hydrogenation only occurs after the most active sites for butadiene retention have been occupied, and most probably after monolayer coverage has been reached. This initially adsorbed monolayer gradually dissociates,

releasing hydrogen for the self-hydrogenation reaction, leaving a dissociatively adsorbed hydrocarbonaceous surface residue.

This phenomenon is observed on the Rh/SiO_2 catalyst as the number of butadiene molecules injected on the first injection (2.6×10^{19} molecules/g.catalyst) is insufficient to saturate all the available sites for adsorption into the monolayer. On the Pt/SiO_2 and Pd/SiO_2 catalysts, which have lower metal surface areas than the Rh/SiO_2 catalyst, the injection size is sufficient to saturate all the available sites for adsorption and self-hydrogenation on the first injection and, therefore, hydrogenated products and butadiene are observed in the eluant from the first injection.

Retention is observed simultaneously with self-hydrogenation following injections made subsequent to the first appearance of hydrogenated products over each catalyst, and indeed retention is often observed following injections in which self-hydrogenation has ceased. This indicates that two (or possibly more) processes are occurring after the completion of the monolayer.

Self-hydrogenation is occurring at certain sites on the catalyst but, as self-hydrogenation generally decreases quite rapidly as increasing numbers of injections are made, the number of sites where this can occur decreases after each injection. Possible reasons for this are depletion of the available hydrogen pool, or poisoning of the active sites by the build-up of inactive carbonaceous residues.

Retention is occurring at different sites from those involved in hydrogenation, which are less quickly deactivated and, indeed, in

several cases retention appears to reach an approximately steady state. Comparison of the values of the cumulative retention of butadiene on the catalysts (tables 4.3, 5.3, 6.3, 7.3) with the estimated numbers of surface metal atoms indicates that retention in excess of that required for monolayer coverage is occurring, indicating that some retained butadiene may not be directly bonded to the metal surface of the catalyst. This 'excess' butadiene cannot be physically adsorbed on the surface, nor is it likely that it is associatively chemisorbed on the surface as, in both cases, the carrier gas flow would remove the butadiene from the surface.

Three possible explanations have been advanced for the retention of hydrocarbon in excess of monolayer coverage on supported metal catalysts. These are adsorption directly on to the catalyst support, surface migration of hydrocarbon adsorbed on the metal to the catalyst support, or polymerisation on the catalyst.

In the course of studies of the adsorption of ^{14}C-ethylene on Rh/Al_2O_3 and Rh/SiO_2, Reid (26) has shown that, in the presence of metal, ethylene adsorbs on both supports, with the adsorption being greater on the alumina. Evacuation for 1 hour was found to remove 62% of the adsorbed ethylene from SiO_2 and 47.5% from Al_2O_3. However, the extent of adsorption on the supports was too small to account for the secondary adsorption observed on Rh/SiO_2 and Rh/Al_2O_3 and, furthermore, the secondary adsorbed ethylene was unaffected by evacuation. Therefore, it was concluded (a) that direct adsorption of ethylene on the supports in the absence of metal was not a sufficient explanation for secondary adsorption, and (b) adsorption of ethylene on support in the presence of the metal would be much less important

on silica-supported catalysts than on alumina-supported catalysts.

The extent of direct adsorption of any unsaturated hydrocarbons on the catalyst support would appear to be generally smaller on silica than on alumina. In an infra-red spectroscopic study of the adsorption of acetylene and acetylene derivations on silica and alumina, Yates and Lucchesi (69) found evidence for two modes of adsorption of acetylene on alumina, one of which, perpendicular to the alumina surface, was strongly adsorbed. On silica, only a small amount of a weakly adsorbed mode, parallel to the surface, was detected, similar to the weakly adsorbed mode on alumina. In the present study, therefore, it is considered that direct adsorption of butadiene on the silica support of the catalysts will be negligible, particularly as the constant flow of the carrier gas will act upon weakly adsorbing species in a similar manner to a vacuum.

Reid et al (26) have proposed that secondary adsorption in excess of that required for metal coverage can be accommodated by means of the migration of adsorbed hydrocarbon species from sites on the metal to sites on the catalyst support.

Surface migration of adsorbed hydrocarbons is implicit in mechanisms discussed for bifunctional catalysts (57). McNab and Webb (58) have suggested that the hydroisomerisation of but-1-ene over Rh/SiO_2 occurs on the support and involves migration of hydrocarbon from the Rh to the support, whilst the hydrogenation occurs solely on the metal.

However, in studies of the adsorption of ^{14}C-ethylene and ^{14}C-acetylene on silica-supported Rh, Ir and Pd and on Pd/Al_2O_3, Al-Ammar

and Webb (29) have shown that secondary adsorption on catalysts which had been treated with hexamethylsilazane, which effectively covered the support surface with trimethylsilyl groups, is the same as on untreated catalysts. As 'spillover' requires the presence of suitable sites on the support, it appears unlikely that secondary adsorption observed by Al-Ammar and Webb can be satisfactorily explained in terms of this phenomenon. Spillover can thus be discounted as giving rise to the associatively adsorbed secondary adsorption proposed by Al-Ammar and Webb, and, if this model is assumed to apply to unsaturated hydrocarbons in general, it is therefore unlikely that spillover of hydrocarbon on to the silica-surfaces of the catalysts has any bearing on the species retained in excess of monolayer coverage of the metal in the present study.

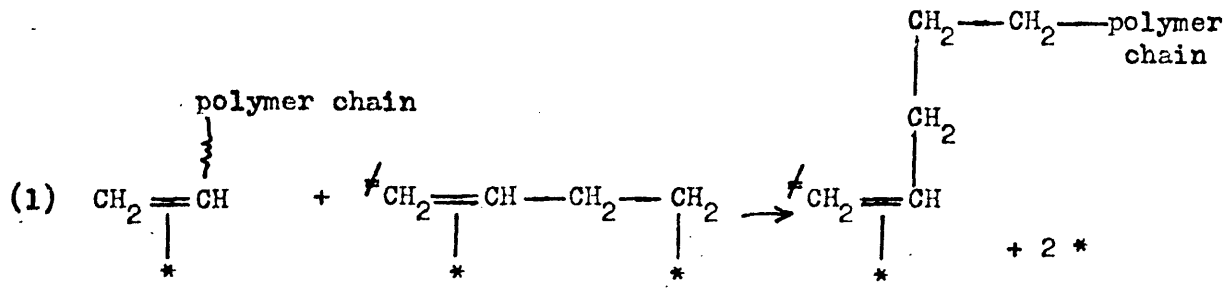
The formation of surface polymers following the adsorption of unsaturated hydrocarbons on both unsupported and supported metal catalysts is well documented. Beeck (70) showed that saturated polymeric species of C_4- to C_8- and higher could be removed from a metal film on which ethylene had been adsorbed by the admission of hydrogen in the gas phase. On Ni, 90% of the removed species were polymeric, but in a similar experiment on a Rh film the bulk of the species removed consisted of ethane and only a small amount of polymeric species was observed.

Altham (71) used thermal desorption techniques to demonstrate the existence of C_3- and higher hydrocarbons retained on the surface following the adsorption of ethylene and/or acetylene on Pt/SiO_2 and Pt/Al_2O_3 catalysts. The hydropolymerisation of acetylene is well known and has been discussed by Bond (66).

Morrow and Sheppard (17) used infra-red spectroscopy to show the presence of n-butyl groups on the surfaces of supported platinum and nickel catalysts following the hydrogenation of ethylene on these catalysts, whilst Avery (19) has interpreted the infra-red spectrum of butadiene adsorbed on silica-supported Pd as being due to the presence of dehydrogenated $(C_4)_n$ polymer units. On admission of hydrogen to the catalyst, the spectrum of the polymeric species, rich in CH_2- groups rather than the CH_3- groups which would be expected for a monomeric species, was recorded on the catalyst surface.

In the study of acetylene and ethylene adsorption on silica-supported Rh, Ir and Pd, and alumina-supported Pd by Al-Ammar and Webb (30) hydropolymerisation on the catalyst surface is proposed as an explanation of catalyst deactivation. In the present study, made in the absence of added molecular hydrogen and therefore with a more limited hydrogen 'pool', deactivation for hydrogenation is rapid, but retention is observed even when hydrogenation has ceased. It is therefore suggested that the retention of butadiene in excess of monolayer coverage is caused by hydropolymerisation occurring on the metal surface, using the hydrogen released by the dissociation of the butadiene on the surface. This hydropolymerisation will also have the effect of rapidly deactivating the catalyst for self-hydrogenation by depleting the pool of available hydrogen. The reaction is envisaged as proceeding by the addition of an associatively adsorbed butadiene molecule or, more probably, a half-hydrogenated intermediate of the type proposed (36, 39) in the hydrogenation mechanisms of Bond et al. and Bates et al., to the growing chain at the point of attachment to the surface. Carbon filament growth has been observed by electron microscopy (72) to proceed in this manner. The mechanism for this is

unknown, but is likely to be an insertion reaction which may be represented as



The half-hydrogenated species shown is formed by addition of hydrogen to an associatively adsorbed molecule of butadiene.

The polymerisation is regarded as occurring on the metal. Olefin polymerisation has been observed on catalyst support materials such as silica (73) and silica-alumina (74), but the mechanism of polymerisation on these materials has required the presence of Bronsted acid sites.

Silica, however, is believed to be neutral and, therefore, whilst some polymerisation on the support may occur in adsorption experiments on alumina-supported catalysts, polymerisation on the silica support of the catalysts used in the present study is unlikely, due to the absence of suitable acid sites.

The extent of polymerisation appears to be less in adsorptions carried out over the freshly reduced Pt/SiO_2 than over the regenerated catalysts, as shown by the low values observed for retention on the second and subsequent injections over these catalysts. The reason for this is unclear, but is probably due to some modification of the surface during the regeneration process. The major difference between the reduction and regeneration processes is that during the regeneration process, unsaturated residues are chemisorbed on the metal surface. Some of these residues are not removed by

hydrogen treatment at high temperature and it may be that the presence of these residues on the surface modifies the surface in some way during the first regeneration, and activates it for the polymerisation process.

Whilst the polymerisation process is going on, the hydrogenation process is also occurring, and would appear to be in competition with the hydropolymerisation process for the available hydrogen pool. The hydrogenation activity is greatest in injections over the freshly reduced Pt catalyst, and the extent of polymerisation is minimal over these catalysts. On the regenerated catalysts however, the competition of the polymerisation process reduces the extent of hydrogenation, particularly for the palladium catalyst which is the least active catalyst for hydrogenation.

The low activity of palladium may be intrinsic as the low value for adsorption of butadiene indicates that the metal surface area may not be as large as expected. The value for the number of surface metal atoms quoted by Orozco (64) refers to a freshly reduced catalyst. The regenerated catalyst will have this slightly reduced by adsorbed surface residues not removed by regeneration, as will the Pt and Rh catalysts, but Pd is readily prone to sintering and this may drastically reduce the available surface area.

n-Butane is formed initially on all catalysts in the present study, and is seen to be formed before the n-butenes on Rh/SiO_2. However, n-butane is not usually formed on the second or subsequent injections except at high temperatures. The formation of n-butane on the palladium catalysts was unexpected in view of the reports of

Bond et al. (36) and Wells et al. (39, 40) which consistently showed palladium to be totally selective for butene formation.

n-Butane is formed before the n-butenes on the Rh catalyst and, as n-butane is the sole product on Pt/SiO_2 at low temperature, it is believed that n-butane formation occurs before n-butene on the Pt catalyst also. Similarly, there is evidence on Rh, that the but-2-enes are formed earlier in a series of injections than but-1-ene. But-1-ene production on Pt and Rh appears to be diminished relative to the but-2-enes following those injections in which n-butane is also formed. The ratio of but-1-ene to but-2-ene is observed to increase with increasing injection number during a series of injections.

These observations would indicate that n-butane is formed on the most reactive sites of the catalyst and the but-2-enes on sites distinct from those for formation of but-1-ene. The sites for n-butane formation however, become depleted in hydrogen very quickly and they are rapidly inactivated either by hydrogen depletion or by build-up of carbonaceous residues. The observed depletion of but-1-ene relative to but-2-ene whilst n-butane is being formed suggests that the formation of n-butane and the formation of but-1-ene are competitive. This competition may arise from several effects. Both n-butane and but-1-ene may be formed on the same sites and therefore may be in direct competition with each other for the hydrogen pool at these sites. n-Butane may also be formed in a 'step-wise' process by the further hydrogenation of but-1-ene on the catalyst surface. This will be discussed further in the light of radiotracer evidence.

The observed trans:cis ratios were normally in the region of 1.1 to 2.1 over the Pt and Rh catalysts, in good agreement with the work of Bond et al. (36) on the alumina-supported catalysts. An extraneously high trans:cis ratio observed following an injection over Rh/SiO_2 at 323K suggests that the active sites for the isomerisation of the half-hydrogenated C_4H_7 intermediate are rapidly deactivated at low temperature.

The trans:cis ratios following injections over the Pd catalyst are difficult to determine at low temperatures, due to the low extent of hydrogenation on these catalysts. However, there is evidence for a general increase in trans:cis ratio with increasing injection number. The trans:cis ratio is in the region 1.5 to 2.0 initially, that is, higher on average than for Pt or Rh, and increases rapidly with subsequent injections, although the indications are that the rate of increase of the trans:cis ratio with injection number is slower at high temperature.

This indicates that, on all three catalysts, sites exist for the isomerisation of either adsorbed butadiene or the half-hydrogenated C_4H_7 intermediate via the mechanism proposed by Bond et al. (36). However, these sites become rapidly deactivated on the Pd catalyst, and on the Rh catalyst at low temperature, inhibiting the isomerisation and hence, raising the yield of trans-but-2-ene relative to the cis-isomer.

A further possibility for the increase in the trans:cis ratio with increasing injection number is that surface migration between a hydrogenation site and an adjacent isomerisation site is inhibited by the accumulation of carbonaceous residues. However, deposition

of carbonaceous residues would be greater at high temperature, due to the greater extent of dissociation indicated by the high hydrogenation activity, and therefore surface migration would decrease as temperature increased. This would inhibit isomerisation and an increase in the trans:cis ratio with temperature would be observed, whilst little or no increase in this ratio with injection would occur.

Instead, as shown by the experimental evidence, the trans:cis ratio on Pd, and on Rh at low temperature, rises with decreasing hydrogen availability (measured by the overall hydrogenation activity), and that this increase is slower at high temperature. This indicates that hydrogen availability is important rather than surface mobility, and this would also indicate that isomerisation of the half-hydrogenated intermediate C_4H_7 is more important in determining trans:cis ratios than isomerisation of syn- and anti- adsorbed butadiene. The sites for the isomerisation of the half-hydrogenated species however, become depleted in hydrogen and become poisoned by the accumulation of dehydrogenated residues. The high trans:cis ratios observed in the hydrogenation of butadiene-hydrogen mixtures (36, 39, 41) can be accommodated in this model by an inability of the gas-phase hydrogen to reactivate these sites under the relatively mild conditions used in these studies (all below 318K), as can the observation by Bates and Wells (40) that the trans:cis ratio drops from 14.4 at 311K to 2.6 at 463K on Pd films.

8.2 The Radiochemical Experiments

Whilst much information can be obtained from an analysis of the product distributions regarding the relative importance of

different types of site, this can be enhanced by a study of the available hydrogen pool and how it interacts with butadiene in the hydrogenation process. There are two possible components of this hydrogen pool, namely, hydrogen evolved from the dissociative adsorption of butadiene on the catalysts and hydrogen associated with the catalyst itself, whether on the metal surface or on the silica support.

Previous workers (50) have shown that, in a flow system of the type used in the present study, the constant flow of the helium carrier gas removes all of the exchangeable hydrogen from the metal surface. Altham and Webb (50) have measured the amount of exchangeable hydrogen on Pt/Al_2O_3 and Pt/SiO_2 catalysts to be (a) in excess of that which could be associated solely with the metal and (b) in good agreement with the value of the surface concentration of hydroxyl groups on both alumina and silica measured by Hall et al. (75).

Each of the three regenerated catalysts was found to show a similar pattern in the tritium exchange reaction. Exchange was, as expected, greatest following the first injection of tritium, and decreased sharply in the next few injections before reaching a point at which the extent of exchange was virtually constant or very slowly decreasing. The shape of the exchange curves indicated that exchange, as measured by the activity of the eluant relative to a standard injection, was unlikely to fall to zero without the injection of some several hundred millilitres of tritium. It was therefore concluded that an approximately steady state had been reached at this point. The nature of this steady-state is unclear but may be analogous to the migration of hydrogen from Ha (I) to Ha (II) sites as

proposed by Paal and Thomson who represented it as

$$H_2 \text{ (gas)} \rightleftharpoons Ha(I) \longrightarrow Ha(II)$$

Exchange was assumed to have effectively ceased at this point since, as Ha(II) does not react with hydrocarbons, the formation of Ha(II) is unimportant in the hydrogenation reaction.

Comparison of the extent of exchange on each catalyst until the steady state was reached show good agreement with the values of the silica surface hydroxyl concentration, measured by Altham (50), to be 1.13×10^{14} cm^{-2}, as shown in table 8.1.

Table 8.1.

Tritium exchange on Pt/SiO_2, Pd/SiO_2 and Rh/SiO_2

Catalyst	μl	Hydrogen Exchange atoms x 10^{-19}/ g.catalyst	Hydrogen Exchange atoms x 10^{-19}/ g.SiO_2	Exchangeable H/cm^{-2} on SiO_2 *
Pt/SiO_2	2048.1	22.028	23.187	1.19×10^{14}
Pd/SiO_2	1135.0	24.416	25.701	1.28×10^{14}
Rh/SiO_2	2153.6	23.162	24.381	1.22×10^{14}

* assuming SiO_2 surface area = 200 $m^2 g^{-1}$

It is suggested that tritium is exchanged on the SiO_2, possibly after initial adsorption on the metal. Once the SiO_2 exchange is complete, some tritium may be retained on the catalyst as the hydrocarbon inaccessible Ha(II) species, which would account for the

steady state observed. A possible exchange scheme might be

(iii) $Ta(I) + {}^{-}OH \rightleftharpoons {}^{-}OT + Ha(I)$

(iv) ${}^{-}OT + Ta(I) \rightleftharpoons Ta(II) + {}^{-}OT$

Equation (iii) represents exchange with the hydroxyl groups on the silica, whereas equation (iv) represents retention of tritium as a non-reactive species. This non-reactive species would not be important in the hydrogenation mechanism, and the metal would be effectively bare of reactive hydrogen in this scheme.

Tritium was found to be incorporated in each of the various components of the reactor eluant following injections of butadiene on to catalyst samples which had been tritium exchanged. This shows that there is a substantial degree of exchange occurring between the hydrogen generated by the initial dissociative adsorption of butadiene and the hydrogen associated with the hydroxyl groups on the silica support.

The tritium content of the hydrogenated products is seen to increase on the second and subsequent injections to reach a maximum value and then decrease. The increase is due to the greater degree of equilibration of the two hydrogen sources during the interval between the injections. However, as hydrogen (from both sources) is used up in hydrogenation, the probability of

$$H(a) + \underset{*}{OT} \rightleftharpoons T(a) + \underset{*}{OH}$$

eventually becomes less than

$$H(a) + \underset{*}{OH} \rightleftharpoons H(a) + \underset{*}{OH}$$

and

$$T(a) + OH \rightleftharpoons H(a) + OT$$

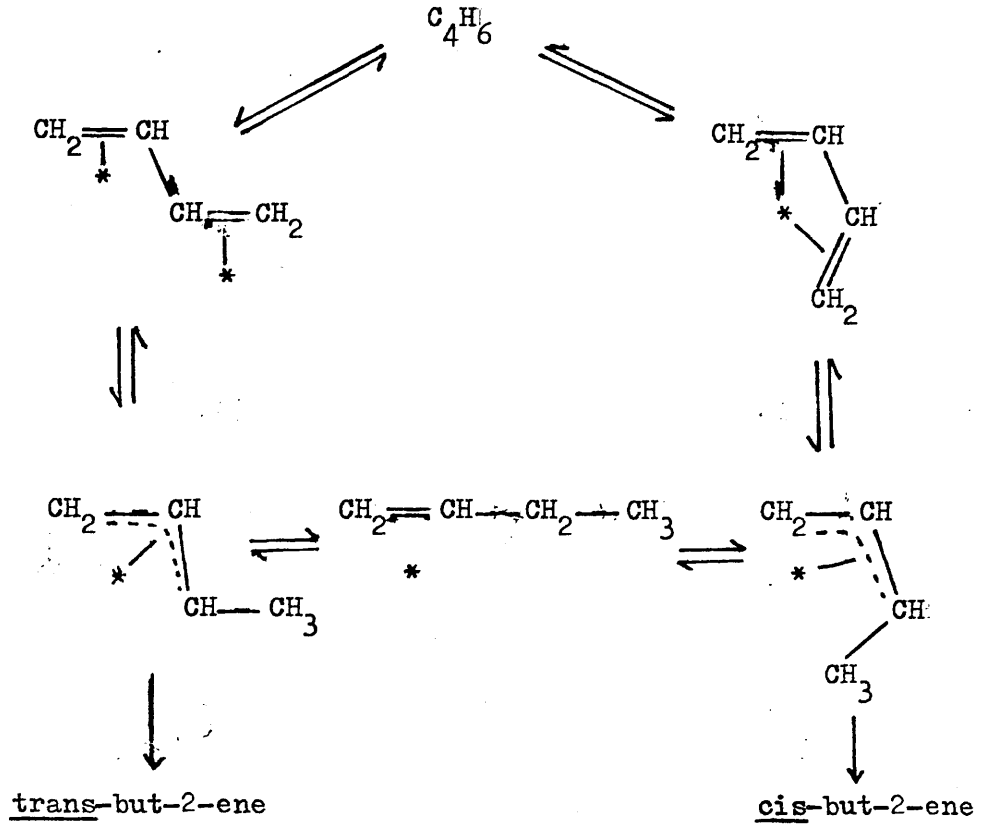
due to the decrease in the concentration of OT groups on the silica, that is, an exchange resulting in tritium replacing protium on the metal surface becomes progressively less probable than an exchange resulting in a protium atom on the metal surface.

The incorporation of tritium in butadiene eluted from the reactor indicates that butadiene adsorbs reversibly. The tritium content of the but-2-enes is generally higher than that of the but-1-ene found following the same injection, and cis-but-2-ene often has a slightly higher tritium content than the trans isomer.

This can be explained in terms of the hydroisomerisation mechanism proposed for the formation of the isomeric but-2-enes. An isomerisation process involving the half-hydrogenated C_4H_7 intermediate introduces the possibility of a greater number of interconversions occurring on the catalyst before final desorption as but-2-ene, and therefore there is a greater probability of hydrogen exchange between the hydrocarbon and the catalyst surface. Also, if the proportions of syn- and anti- adsorbed butadiene bear any relation to their proportions in the gas phase, a greater proportion of the cis-but-2-ene than the trans-isomer must necessarily be derived from the hydro-isomerisation process, which will involve the possibility of a greater number of interconversions than will direct 1,4-addition, and thus cis-but-2-ene would have a higher tritium content than trans-but-2-ene.

As this effect is observed on all three catalysts, it is likely that the hydroisomerisation process, proposed initially for Pd, contributes to the formation of the isomeric but-2-enes on each of the catalysts.

A possible mechanism for but-2-ene formation is shown below.



The relative extents of the sequential hydrogen addition and the hydroisomerisation and addition processes determine the relative yields of the two isomeric but-2-enes. The isomerisation step is shown as proceeding through a mono-π-adsorbed species as the π-allylic adsorbed species are locked into their configurations by the π-allylic bond.

As previously stated, the isomerisation sites on Pd become rapidly depleted in hydrogen and the yield of trans-but-2-ene relative to the cis isomer increases rapidly as the extent of isomerisation decreases. On Pt and Rh, regeneration of the isomerisation sites occurs more readily, by hydrogen migration during self-hydrogenation

or by gas-phase hydrogen during hydrogenation of butadiene/hydrogen mixtures, than it does on Pd.

The observed tritium content of n-butane found concomitantly with the n-butenes did not bear any obvious relationship to the tritium content of the n-butenes. This suggests that the n-butane is formed on different types of active sites, where the equilibration of protium from dissociative adsorption with tritium on the silica is different, from those involved in the formation of butenes. If it had been formed on the same sites as one of the n-butenes, the tritium content would be expected to be approximately twice that of the butene in question. The tritium content of the n-butane, relative to that of each of the n-butenes, varies widely and irregularly. This may indicate the direct formation of n-butane from butadiene, but formation of n-butane by the hydrogenation of previously formed but-1-ene cannot be discounted, if the second hydrogenation occurs at a different site from the initial hydrogenation to but-1-ene.

The tritium content of the n-butane relative to the butenes is temperature dependent, being much higher at high temperatures than at low. This indicates that exchange between hydrogen and tritium, and/or between the hydrocarbon and the catalyst, are activated processes, and occur more rapidly at high temperatures. The low tritium content of n-butane at low temperatures is due to the n-butane being formed, at the most reactive hydrogenation sites, before the n-butenes and therefore before the equilibration of hydrogen and tritium has progressed to the same point as during the formation of the n-butenes.

As discussed earlier, the behaviour of the Rh catalyst differed from the Pt and Pd catalysts in the ease with which carbon-carbon bond

fission occurred. Methane is virtually the sole product of this process, and it is formed before hydrogenation begins, concomitantly with the initial adsorption of butadiene. As the tritium content of the methane is low, hydrogen from the dissociation of butadiene also plays a large part in the cracking process. Methane production ceases as hydrogenation begins, indicating that hydrogenation can only occur once a sufficiently large amount of the catalyst surface has been covered in adsorbed hydrocarbon, which will eventually form a dissociatively adsorbed monolayer as the self-hydrogenation process goes on. It is observed that methane production and n-butane formation are competitive, n-butane yield being greatest when methane is minimal and vice-versa.

This suggests that the same sites are involved in both processes. At high temperatures, methane production occurs initially, but once methane production stops, possibly due to lack of available metal surface, associatively adsorbed butadiene is hydrogenated to n-butane on the same sites, although the available hydrogen pool has been depleted by the methane formation, and thus n-butane yield is reduced compared to that observed at low temperatures, where the extent of methane formation is low.

8.3. General Conclusions

The three catalysts used in the present study show similar features in their interaction with butadiene, and it is suggested that they all follow the same general scheme of adsorption and self-hydrogenation.

Following the initial injections of butadiene, the metal surface of the catalyst becomes covered in adsorbed butadiene. This

adsorbed butadiene progressively dissociates, liberating adsorbed hydrogen, and eventually forms a dissociatively adsorbed monolayer.

The adsorbed hydrogen liberated by this process immediately begins to exchange with hydrogen already present on the catalyst, which is associated with the silica support as hydroxyl groups.

At high temperatures, the initial adsorption of butadiene on the Rhodium-silica catalyst is accompanied by the formation of methane, indicating that the process of dissociation occurs much more quickly on rhodium than on the other two catalysts. It also indicates that the monolayer, when formed, is not necessarily composed exclusively of C_4- species.

Both self-hydrogenation and retention processes occur on the catalysts. Retention of butadiene, in excess of that which can be attributed to a monolayer coverage, occurs by hydrocarbon insertion reactions on active sites to form surface polymers. The polymerisation process occurs even when self-hydrogenation has ceased, and is likely to proceed by hydropolymerisation, using hydrogen derived from dissociative adsorption, and thus competes with the self-hydrogenation process. Both the hydropolymerisation process and the self-hydrogenation process accelerate the dissociation of the initially adsorbed butadiene by their demand for hydrogen.

Self-hydrogenation occurs in competition with the hydroisomerisation process, but hydropolymerisation usually continues to be observed after self-hydrogenation has ceased. This indicates that the active sites for the two processes are different, and that those for self-hydrogenation are more rapidly deactivated due to the accumulation of carbonaceous residues.

n-Butane is formed at highly reactive sites on rhodium, and probably on platinum, before the n-butenes are formed, indicating that different sites are probably involved. Some n-butane is also formed at high temperature on palladium. On rhodium, n-butane formation is inhibited by the cracking reaction to form methane at high temperatures.

All three n-butenes are formed over each catalyst, with but-1-ene being the most abundant butene except at high temperatures on rhodium, and when the n-butane yield is high. This may indicate that a proportion of the n-butane is formed by further hydrogenation of but-1-ene.

The isomeric but-2-enes are found to occur in low trans:cis ratios on all three catalysts, and the ratio increases as the available hydrogen pool is depleted, indicating that isomerisation of the half-hydrogenated C_4H_7 species is occurring. On palladium, the sites for this isomerisation are readily deactivated, particularly at low temperatures, giving rise to much higher trans:cis ratios in the later injections of a series.

REFERENCES

1. P. Sabatier and J. P. Senderens, Compt. Rends., 135, 87, (1902).
2. I. Langmuir, J.Amer.Chem.Soc., 38, 2270, (1916).
3. S. E. Lennard-Jones, Trans. Faraday Soc., 28, 333, (1932).
4. G. Halsey and H. S. Taylor, J. Chem. Phys., 15, 624, (1947).
5. P. M. Grundy and F. C. Tompkins, Quart. Rev., 14, 257, (1960).
6. J. K. Roberts, Proc. Roy. Soc., A152, 445, (1935).
7. G. K. L. Cranstoun and S. J. Thomson, Trans. Faraday Soc., 59, 2403, (1963).
8. H. S. Taylor, Proc. Roy. Soc., A108, 105, (1925).
9. J. M. Thomas, Adv. Catalysis, 19, 293, (1969).
10. A. T. Gwathmey and R. E. Cunningham, Adv. Catalysis, 10, 57, (1958).
11. L. Whalley, B. J. Davis and R. L. Moss, Trans. Faraday Soc., 66, 3143, (1970).
12. B. Lang, R. Joyner and G. A. Somorjai, J. Catalysis, 27, 405, (1972).
13. D. W. Blakeley and G. A. Somorjai, J. Catalysis, 42, 181, (1976).
14. S. J. Thomson and G. Webb, J. Chem. Soc. Chem. Commun., (1976), 526.
15. R. P. Eischens, W. A. Pliskins and S. A. Frances, J. Chem. Phys., 22, 1786, (1954).
16. R. P. Eischens and W. A. Pliskin, Adv. Catalysis, 10, 1, (1958).
17. B. A. Morrow and N. Sheppard, J. Phys. Chem., 70, 2406, (1960).
18. B. A. Morrow and N. Sheppard, Proc. Roy. Soc., A311, 391, 415 (1969).
19. N. R. Avery, J. Catalysis, 19, 15, (1970).

20. H. A. Peirce and N. Sheppard, Surf. Sci., 59, 205, (1976).

21. D. W. McKee, J. Amer. Chem. Soc., 84, 1109, (1962).

22. S. J. Stephens, J. Phys. Chem., 62, 714, (1958).

23. J. R. Arthur and R. S. Hansen, J. Chem. Phys., 36, 2062, (1962).

24. G. A. Somorjai, Adv. Catalysis, 26, 1, (1977).

25. D. Cormack, S. J. Thomson and G. Webb, J. Catalysis, 5, 224, (1966).

26. S. U. Reid, S. J. Thomson and G. Webb, J. Catalysis, 29, 421, (1973).

27. G. F. Taylor, S. J. Thomson and G. Webb, J. Catalysis, 12, 191, (1968).

28. A. S. Al-Ammar, S. J. Thomson and G. Webb, J. Chem. Soc. Chem. Commun., (1977), 323.

29. A. S. Al-Ammar and G. Webb, J. Chem. Soc., Faraday I, 74, 195, (1978).

30. A. S. Al-Ammar and G. Webb, J. Chem. Soc., Faraday I, 74, 657, (1978).

31. J. U. Reid, S. J. Thomson and G. Webb, J. Catalysis, 29, 433, (1973).

32. Y. Inoue and I. Yasumori, J. Phys. Chem., 73, 1618, (1969).

33. J. J. Rooney, J. Catalysis, 2, 53, (1963).

34. J. J. Rooney and G. Webb, J. Catalysis, 3, 488, (1964).

35. J. D. Prentice, A. Lesiunas, N. Sheppard, S. Chem. Soc. Chem. Commun., (1976), 76.

36. G. C. Bond, G. Webb, P. B. Wells and J. M. Winterbottom, J. Chem. Soc., (1965), 3218.

37. B. J. Joice, J. J. Rooney, P. B. Wells and G. R. Wilson, Discuss. Faraday Soc., 41, 223, (1966).

38. J. J. Phillipson, P. B. Wells, and G. R. Wilson, J. Chem. Soc. (A), (1969), 1351.

39. A. J. Bates, Z. K. Leszczynski, J. J. Phillipson, P. B. Wells and G. R. Wilson, J. Chem. Soc. (A), (1970), 2435.

40. P. B. Wells and A. J. Bates, J. Chem. Soc. (A), (1968), 3064.

41. E. F. Meyer and R. L. Burwell, J. Amer. Chem. Soc., 85, 2881, (1963).

42. G. C. Bond, Trans. Faraday Soc., 52, 1235, (1956).

43. J. J. Rooney and F. E. Shephard, J. Catalysis, 3, 129, (1964).

44. J. W. Hightower and C. Kemball, J. Catalysis, 4, 363, (1965).

45. P. A. Compagnon, C. Hoong-Van and S. J. Teichner, Proc. Sixth International Congress on Catalysis (1976), Volume 1, page 117, The Chemical Society, 1977.

46. D. A. Dowden in Chemical Society Specialist Periodical Reports, 'Catalysis', 3, p. 136 , The Chemical Society, 1980.

47. J. H. Sinfelt and P. J. Lucchesi, J. Amer. Chem. Soc., 85, 3365, (1963).

48. G. C. Bond and P. A. Sermon, J. Chem. Soc. Faraday I, 72, 745, (1976).

49. See Ref. 48 in G. Webb, Chem. Soc. Specialist Periodical Reports, 'Surface and Defect Properties of Solids', 6, p.148 , The Chemical Society, 1974.

50. J. A. Altham and G. Webb, J. Catalysis, 18, 133, (1970).

51. K. C. Campbell and J. Mooney, J. Chem. Soc. Faraday I, 76, 2322, (1980).

52. S. D. Mellor, W. C. Smith and P. B. Wells, Ref. 48 in P. B. Wells, Chemical Society Specialist Periodical Reports, 'Surface and Defect Properties of Solids, 1, p.236, The Chemical Society, 1971.

53. S. D. Mellor and P. B. Wells, Trans. Faraday Soc., 65, 1873, (1969).

54. P. B. Wells and G. R. Wilson, J. Catalysis, 9, 70, (1967).

55. P. B. Wells, J. Catalysis, 52, 498, (1978).

56. Z. Paal and S. J. Thomson, J. Catalysis, 30, 96, (1973).

57. G. A. Mills, H. Heinemann, T. H. Milliken, A. G. Oblad, Ind. and Eng. Chem., 45, 135, (1963).

58. J. I. Macnab and G. Webb, J. Catalysis, 26, 226, (1972).

59. J. U. Reid, J. Catalysis, 30, 372, (1973).

60. J. U. Reid, J. Catalysis, 30, 378, (1973).

61. R.J. Kokes, H. Tobin and P. Emmet, J. Amer. Chem. Soc., 77, 5860, (1955).

62. F. Schmidt-Bleek and F.S. Rowland, Analytical Chem., 36, 1695, (1964).

63. G. F. Taylor, Ph.D. Thesis, The University of Glasgow, 1967.

64. J. M. Orozco-Bermudez, Ph.D. Thesis, The University of Glasgow, 1979.

65. J. U. Reid, Ph.D. Thesis, The University of Glasgow, 1971.

66. G. C. Bond in 'Catalysis by Metals', Chapters 11 and 12, Academic Press, London, 1962.

67. P. Selwood, J. Amer. Chem. Soc., 83, 2853.

68. G. Webb in Comprehensive Chemical Kinetics, 20, 1, (1978).

69. D. J. C. Yates and P. J. Lucchesi, J. Phys. Chem., 67, 1197, (1963).

70. O. Beeck, Discuss. Faraday Soc., 8, 118, (1950).

71. J. A. Altham, Ph.D. Thesis, The University of Glasgow, 1970.

72. J. A. Cairns, AERE Harwell, Personal Communication.

73. Y. Amenomiya, J. H. B. Chenier, and R. J. Cvetanovic, Proc. 3rd. Int. Congress on Catalysis (19), Volume 2, p.1135.

74. J. N. Finch and A. Clark, J. Catalysis, 13, 147, (1969).

75. K. Hall, H. P. Leftin, F. J. Cheselke and D. E. O'Reilly, J. Catalysis, 2, 506, (1963).